Appendices

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Appendix 1

SOP – Sample Collection for Treatability Tests

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Sample Collection for Treatability Tests

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for Sample Collection for Treatability Tests. Sampling locations are discussed in the Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003). Samples will include sediment samples in quantities ranging from 40 gallons (170 L) to 100 gallons (360 L), and 2,200 gallons (8,400 L) of water.

Surface water samples will be collected from throughout the treatability studies program on an as-needed basis for each test. The water sampling station will be located at River Mile 187.5. Composite sediment samples will be prepared from sediments at locations designated S1, S2, S3, and S4. These locations are shown on figures 4 through 10, included in the TS Work Plan.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (BBL, 2003);
- Sampling containers for aqueous samples;
- GPS locator;
- Sampling pump (optional);
- Vibra-coring device;
- 3-inch (outside diameter [o.d.]) by 60-inch aluminum coring tubes; and
- Field notebook.

III. Health and Safety Considerations

Refer to the Revised HASP (BBL, 2003).

IV. Sample Collection for Treatability Tests Procedure

Eight general sampling sites are discussed in the TS Work Plan. Discrete cores will be collected within each sampling site over an area of approximately one-quarter acre (this area would be approximately equivalent to the area covered by a mechanical dredge filling one barge). Record general weather conditions relevant to sample integrity.

Sample collection procedures for water samples are described below:

Surface water samples will be collected from the Thompson Island sampling station located at River Mile 187.5, approximately one foot below the water surface. It is not anticipated that surface water will be collected

in conjunction with the baseline monitoring activities. Water samples will be collected throughout the treatability studies program on an as-needed basis for each test, to avoid difficulties associated with shipment and storage of large volumes of water. During performance of the column studies, it is anticipated that approximately 185 gallons (700 L) will be required weekly for three weeks. For other studies, it is anticipated that less than 50 gallons (180 L). of water will be required weekly.

Sample collection procedures for sediment samples are described below:

1. Obtain target composite sample size from the TS Work Plan for the 1/4-acre Treatability Studies sample location. Calculate target subsample sizes and number of coring tubes per subsample.

2. After the vessel is positioned for subsampling, take GPS location readings. Then proceed with sampling.

3. Obtain subsamples by vibracoring following the SOP for Sediment Core Collection in Appendix 1 of the SSAP QAPP (QEA and ESI, 2002.). Record number of subsamples taken from each position. Chill to 4^{o}C. BBL will provide the core depth to be sampled at each location. It is expected that core depths will be 10 feet or less.

4. Label each core and process for shipment to treatability studies processing laboratory.

Repeat subsampling until all compositing locations are complete. Then move to the next 1/4-acre sampling location and complete all subsampling. Continue until all eight 1/4-acre samples are completed. Record any deviations from this SOP during sampling.

Sample Homogenization Procedures:

1. Place sediments to be homogenized in an appropriately sized, decontaminated, mixing device, such as a cement mixer.

2. Mix for at least 10 minutes, until sediments are combined to a uniform consistency with no unmixed agglomerations of sediment visible.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

QEA and ESI. 2002. *Sediment Sampling and Analysis Program - Quality Assurance Project Plan* (SSAP-QAPP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 2

SOP – Dredged Material Slurry Simulations

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Dredged Material Slurry Simulations

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for preparing Dredged Material Slurry Simulations for use in treatability studies, as described in the Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003). Composite samples or subsamples are delivered to the treatability testing laboratory from the sampling team. Samples are refrigerated (4 degrees C) until preparation of Dredged Material Slurry Simulations.

Samples include water samples and sediment samples in quantities ranging from 8 gallons (31 L) to 550 gallons (2100 L). Water samples will be obtained from the Thompson Island sampling station located at river mile (RM) 187.5 on an as-needed basis during the treatability studies. Composite sediment samples will be prepared from sediment subsamples at locations designated S1, S2, S3, and S4.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- Clean sample containers (8 to 100 gal [31 to 375 L]);
- Variable-speed mixers and motors, as needed to prepare composite samples and dredged material slurry simulations; and
- Laboratory notebook.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Preparation of Dredged Material Slurry Simulations Procedure

Twelve (12) Dredged Material Slurry Simulations are described in the TS Work Plan. These are to be prepared from four sediment categories to evaluate the range of sediment properties which must be accommodated by the material handling and treatment facilities. These are designated:

- S1 = Coarse-grained sediment (assumed to have relatively low PCB concentrations);
- S2 = Mixture of coarse- and fine-grained sediment (assumed to have moderate PCB concentrations);
- S3 = Fine-grained sediment (assumed to have relatively high PCB concentrations); and
- S4 = Fine-grained sediment with oils (assumed to have the highest PCB concentrations).

Water sample composites are to be acquired from a designated location which is routinely monitored by GE; water from this location will be designated as Water Monitoring Site Composite (WMSC).

Dredged material slurry simulations will be prepared by mixing sediment samples with varying quantities of river water to simulate three dredging conditions (one simulation of mechanical dredging, one simulation of mechanically-dredged material transported hydraulically, and one simulation of hydraulic dredging), and designated as follows:

- M1 = sediment to water ratio of 80:20 (volumetric proportions) to simulate mechanically-dredged material with typical amount of entrained water;
- H1 = sediment solids to water ratio of 25:75 (weight proportions) to simulate high-solids content mechanically-dredged material transported hydraulically; and
- H2 = sediment solids to water ratio of 5:95 (weight proportions) to simulate typical-solids content hydraulically-dredged material.

These three dredged material slurry simulations will be prepared for each of the sediment environment conditions, producing dredged material slurry simulations designated as:

- M1S1, H1S1, and H2S1 will be prepared from Sediment S1 and Hudson River WMSC;
- M1S2, H1S2, and H2S2 will be prepared from Sediment S2 and Hudson River WMSC;
- M1S3, H1S3, and H2S3 will be prepared from Sediment S3 and Hudson River WMSC; and
- M1S4, H1S4, and H2S4 will be prepared from Sediment S4 and Hudson River WMSC.

Sediment and water quantities required are listed on lines associated with DQO 1a. and DQO 1b. on Table 2 in the TS Work Plan. Prepare the following mixtures (note the precise weights of the sediment samples being used for these mixtures are a function of the water content of the samples and will be developed after the collection and compositing process is complete):

10 L of M1S1 from 8 L of S1 and 2 L of WMSC;
543 Kg of H1S1 from 136 Kg of S1 and 407 Kg of WMSC; and
775 Kg of H2S1 from 39 Kg of S1 and 736 Kg of WMSC.

10 L of M1S2 from 8 L of S2 and 2 L of WMSC;
115 Kg of H1S2 from 29 Kg of S2 and 86 Kg of WMSC; and
561 Kg of H2S2 from 28 Kg of S2 and 533 Kg of WMSC.

10 L of M1S3 from 8 L of S3 and 2 L of WMSC;
656 Kg of H1S3 from 164 Kg of S3 and 492 Kg of WMSC; and
675 Kg of H2S3 from 34 Kg of S3 and 641 Kg of WMSC.

10 L of M1S4 from 8 L of S4 and 2 L of WMSC;
608 Kg of H1S4 from 152 Kg of S4 and 456 Kg of WMSC; and
659 Kg of H2S4 from 33 Kg of S4 and 626 Kg of WMSC.

The appropriate volumes of sediment and water should be placed in an appropriately-sized glass-lined container and mixed for five minutes with a laboratory mixer. The slurry should be mixed to a uniform consistency, with no unmixed agglomerations of sediment visible.

Note that prior to use of M1 slurries in treatability tests the sample will be allowed to settle for 30 minutes and the free liquid at the top of the sample will be decanted and discarded, a step designed to simulate the settling that will occur during barge transport of mechanically dredged material. Slurry simulations H1 and H2 will be

remixed prior to any use with no settling or decanting of water allowed prior to use in subsequent treatability tests.

Label each container with mixture designation and preparation date of mixture. Keep mixtures refrigerated at 4 degrees C until used in treatability studies.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 3

SOP – Dredge Elutriate Tests

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Dredging Operations Technical Support Program

Contract Report D-95-1
August 1995

Dredging Elutriate Test (DRET) Development

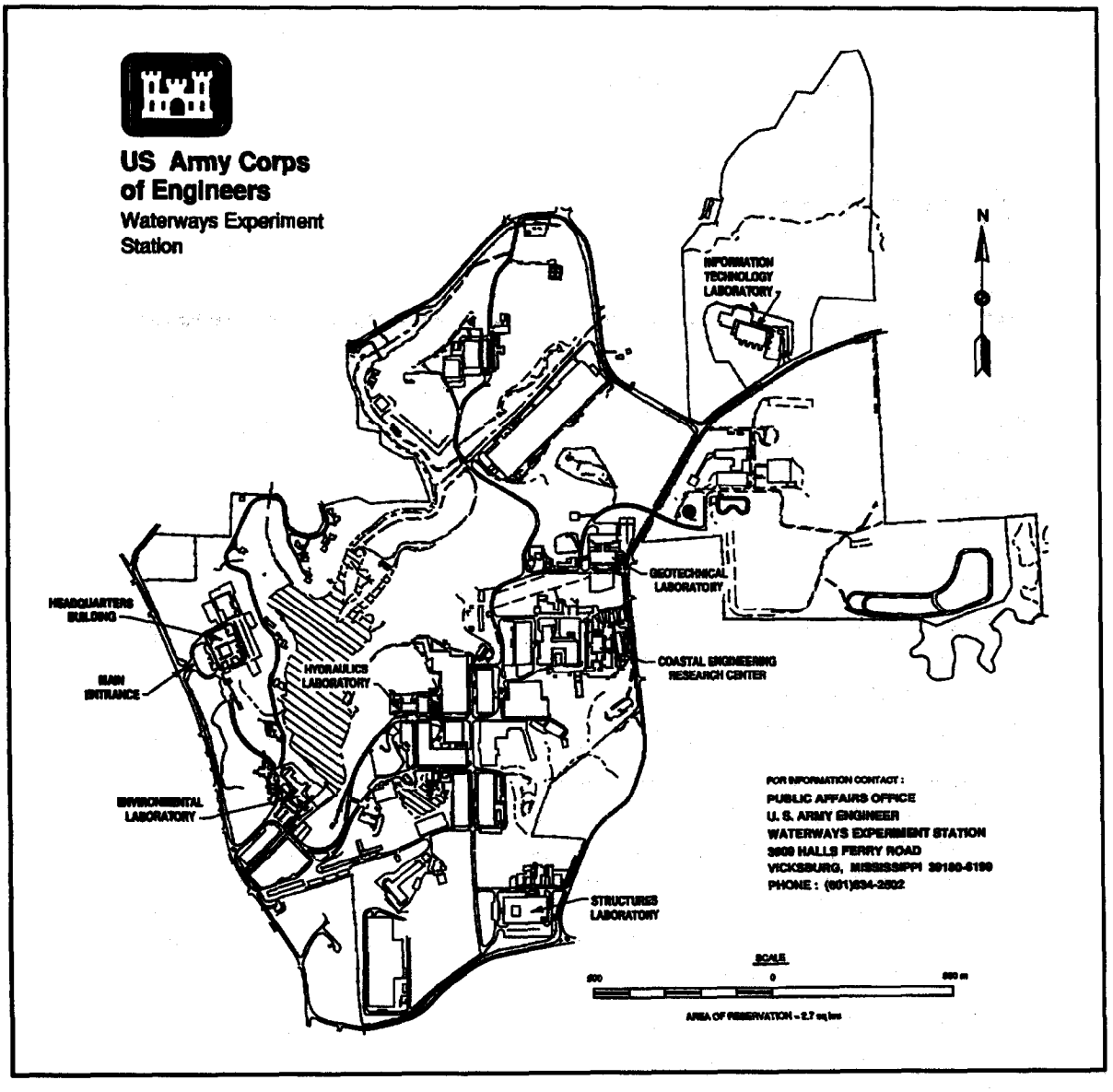
by Francis A. DiGiano, Cass T. Miller, Jeyong Yoon

Department of Environmental Sciences and Engineering
University of North Carolina
Chapel Hill, NC 27599

Final report

Approved for public release; distribution is unlimited

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

Contents

Preface vii

1—Introduction 1

Objectives 2
Background 2

2—Methods 5

Dredging Elutriate Test (DRET) 5
Analytical Methods 7
Site and Field Tests 7

3—Evaluation of DRET Protocol 9

Volatilization of PCB During the DRET 9
Sediment and Water Characteristics 9
Total Suspended Solids and PCB from DRET 11
Metals from DRET 13
Batch Shaker Test 15
Distribution of Sorbed PCB with Particle Size 16
Correlation of Final TSS and DRET Conditions 18

4—Fields Results 24

Field Data from New Bedford Harbor 24
PCB and TSS Data 24
Metals Data 30
Comparison of Field and DRET Results 37

5—Investigation of Particle Size Characteristics 43

Changes in Particle Size Characteristics During Settling in the DRET 43
Settling Characteristics of Particles 48

6—Application of Equilibrium Partitioning Model 53

Development of the Model 53
Usefulness of the Model 56

7—Conclusions and Recommendations 59
Conclusions 59
Recommendations 61
References 62
Appendix A: Analytical Methods A1
SF 298

List of Figures

Figure 1. Steps in development of DRET protocol 6
Figure 2. New Bedford Harbor area map 8
Figure 3. Number PSD for wet-sieved samples 17
Figure 4. Volume PSD for wet-sieved samples 17
Figure 5. Comparison of TSS_f measurement by gravimetric method to TSS_f measurement by PSD method. 21
Figure 6. TSS_f as a function of time after a 1-hr aeration time 22
Figure 7. TSS_f surface as a function of settling time (t_s) and initial suspended solids concentration (TSS_i) 23
Figure 8. Field sample location map 25
Figure 9. Comparison of sorbed PCB for dredgehead samples 29
Figure 10. Comparison of sorbed PCB for plume samples 29
Figure 11. Sorbed Cu concentrations as a function of dredgehead type 36
Figure 12. Sorbed Cd concentrations as a function of dredgehead type 36
Figure 13. Sorbed Pb concentrations as a function of dredgehead type 37
Figure 14. Comparison of PCB concentrations for field dredgehead samples, DRET, and SET results 40
Figure 15. Comparison of PCB concentrations for field plume samples, DRET, and SET results 41
Figure 16. Relationship between total PCB and TSS concentrations 41
Figure 17. Volume PSD as a function of settling time 44
Figure 18. Log-normal PSD as a function of settling time 44
Figure 19. Volume PSD as a function of TSS_i concentration 45

Figure 20. Volume PSD as a function of aeration time 46
Figure 21. Log-normal PSD as a function of aeration and settling times 46
Figure 22. Log-normal PSD as a function of settling time 49
Figure 23. Settling behavior for TSS_i concentrations of 0.5 g/ℓ 51
Figure 24. Settling behavior for TSS_i concentrations of 10 g/ℓ 51
Figure 25. Comparison of observed settling characteristics and Stoke's law predictions 52
Figure 26. Comparison of measured and predicted soluble PCB concentrations 57
Figure 27. Comparison of measured and expected total PCB concentrations 58
Figure A1. Schematic diagram of PSD analyzer A5

List of Tables

Table 1. Predicted Suspended Solids Concentration 4
Table 2. Sediment and Water Characteristics 10
Table 3. PCB Concentration Quantification Method Comparison 11
Table 4. Comparison of Extraction Methods for Determining Sediment PCB Concentrations 11
Table 5. PCB Concentration Summary from DRETs 12
Table 6. PCB Concentration Detail from DRETs 14
Table 7. Metals Concentrations from DRETs 15
Table 8. Release of PCB in Duplicate Batch Shaker Test 15
Table 9. Particle Characteristics Before and After Wet Sieving 18
Table 10. Design of Three-Factor Experiments 19
Table 11. TSS_f as a Function of TSS_i and Aeration Time 20
Table 12. TSS_f as a Function of Settling Time 20
Table 13. Regression Model Parameter Estimates 22
Table 14. Summary of PCB Data from New Bedford Harbor Pilot Study 26
Table 15. TSS and PCB Concentrations for Individual Dredgehead Samples 27
Table 16. TSS and PCB Concentrations for Individual Plume Samples 28

Table 17. Aroclor Detail for Dredgehead Samples 31
Table 18. Metals Data from Dredgehead Samples 34
Table 19. Summary Comparison for Cutterhead Dredge 38
Table 20. Summary Comparison for Horizontal Auger Dredge 38
Table 21. Summary Comparison for Matchbox Dredge 39
Table 22. Particle Size Characteristics as a Function of Settling Time 45
Table 23. Particle Size Characteristics as a Function of Initial Suspended Solids Concentration 47
Table 24. Particle Size Characteristics as a Function of Aeration Time 47
Table 25. β Values From Power-Law Regression 49
Table 26. Composition of PCB Mixture and K_{ow} Values 55
Table 27. Equilibrium Model Predictions of PCB Concentrations 56
Table A1. Atomic Absorption Conditions A3

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.

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

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:

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

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:

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

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).

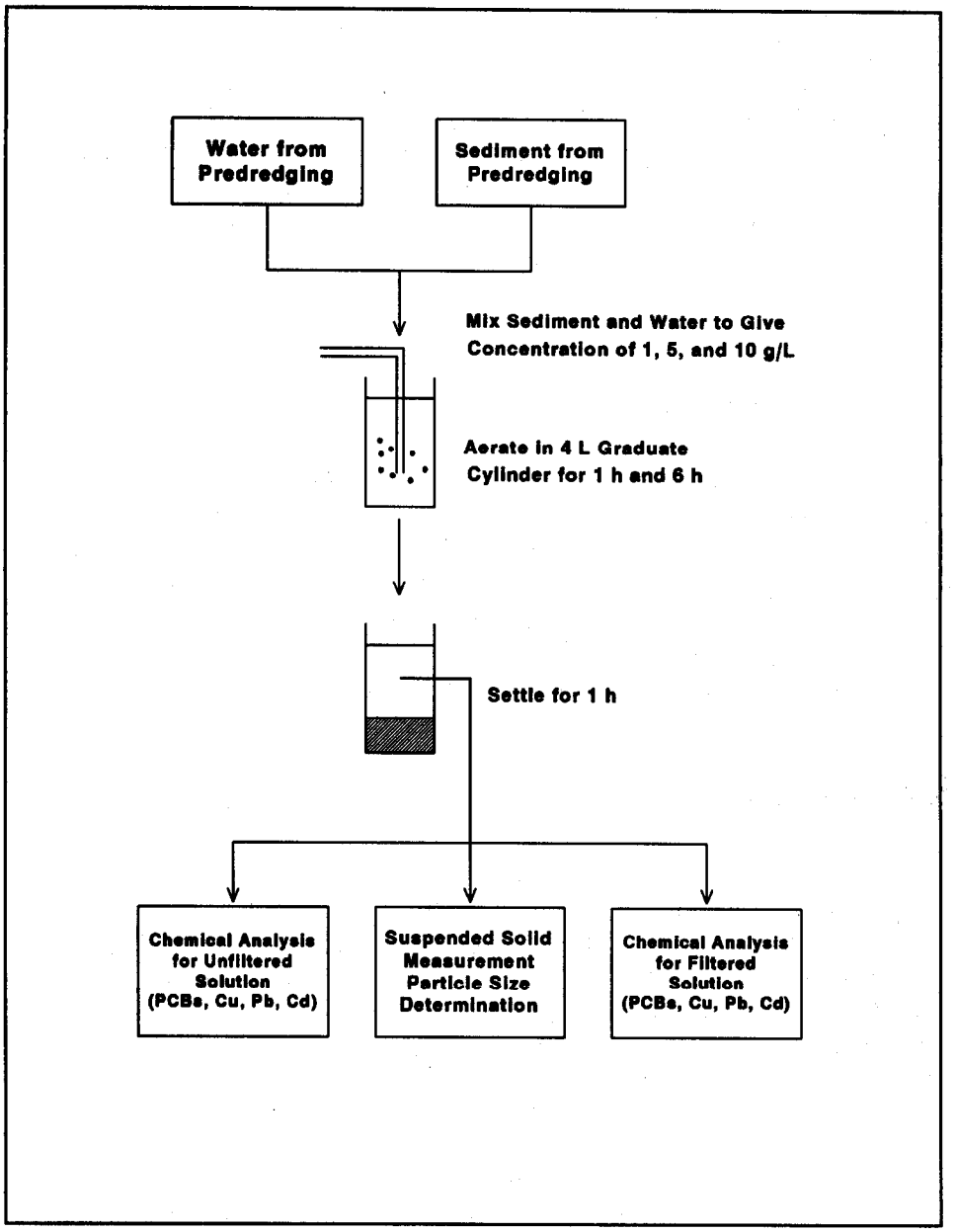


Figure 1. Steps in development of DRET protocol

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.

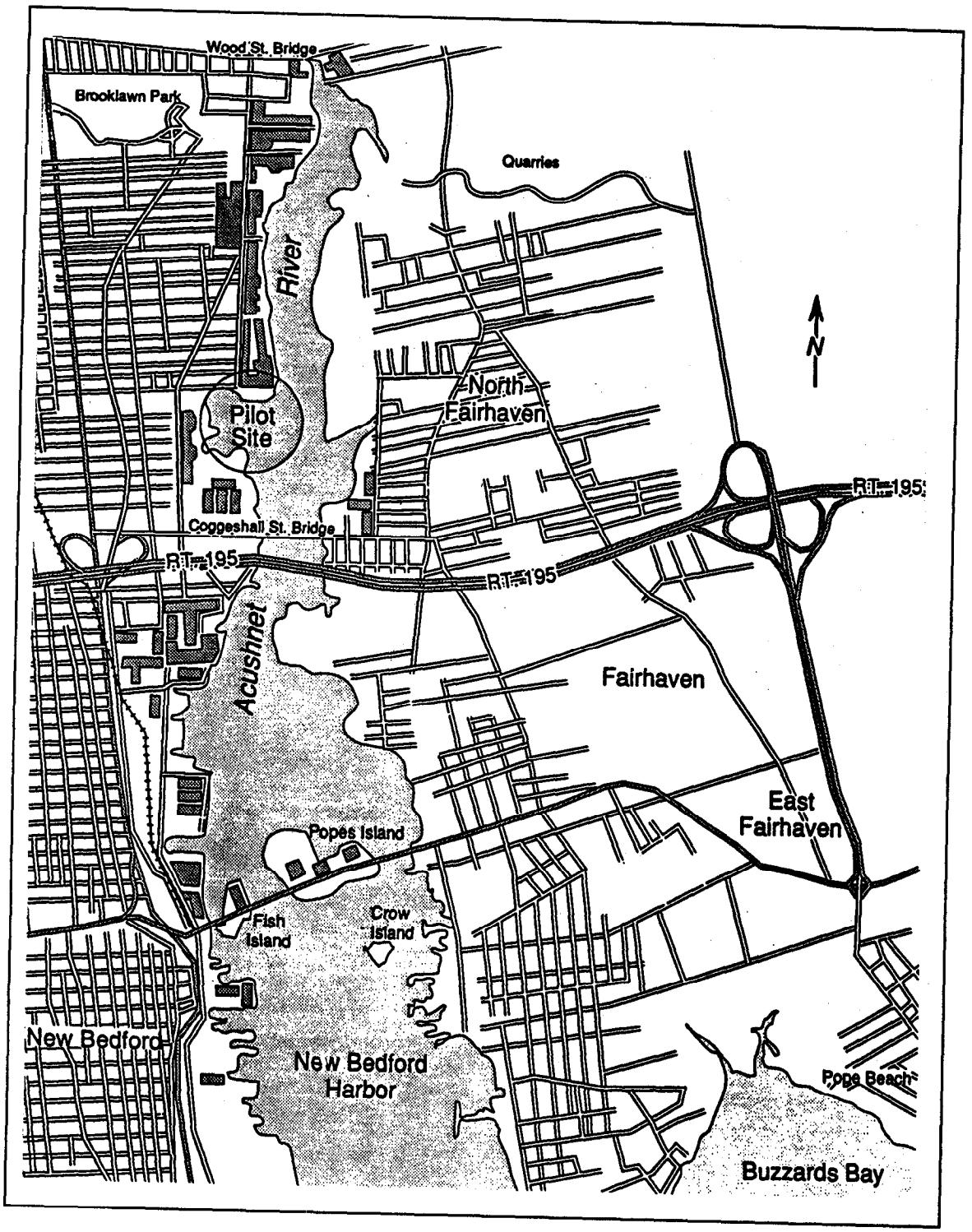


Figure 2. New Bedford Harbor area map

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, 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 6
PCB Concentration Detail from DRETs

TSS_i g/ℓ	Final TSS mg/ℓ	PCB Concentrations									
		Filtered Solution µg/ℓ		Unfiltered Solution µg/ℓ		PCB on Filter µg/ℓ Solution		Sorbed PCB µg/g[a]		Calculated Sorbed PCB, µg/ℓ[b]	
		1242	1254	1242	1254	1242	1254	1242	1254	1242	1254
1-hr Mixing, 1-hr Settling											
1.0	63	2.0	1.0	6.2	4.0	10.3	2.9	163.5	46.0	66.7	47.6
5.0	172	1.6	ND[c]	9.8	6.1	8.6	6.3	50.0	36.6	47.7	35.5
5.0[d]	167	0.4	ND	9.0	4.6	8.6	3.9	51.5	23.4	51.8	27.5
10.0	81	1.8	1.2	6.5	3.7	4.1	3.8	50.6	46.9	58.0	30.9
6-hr Mixing, 1-hr Settling											
1.0	60	NA[e]	NA	3.2	3.0	NA	NA	NA	NA	NA	NA
4.7	104	0.9	0.2	3.5	4.7	3.1	3.3	29.8	31.7	31.9	36.4
5.0	111	1.2	1.2	7.7	5.0	4.1	3.8	36.9	34.2	58.6	34.2
10.0	125	1.3	1.2	4.2	3.5	4.8	5.2	38.0	41.3	23.0	17.6

[a] Measured from fraction retained on filter.
[b] Calculated difference of unfiltered PCB less filtered PCB.
[c] ND = Not detectable.
[d] Duplicate sample.
[e] NA = Not available.

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).

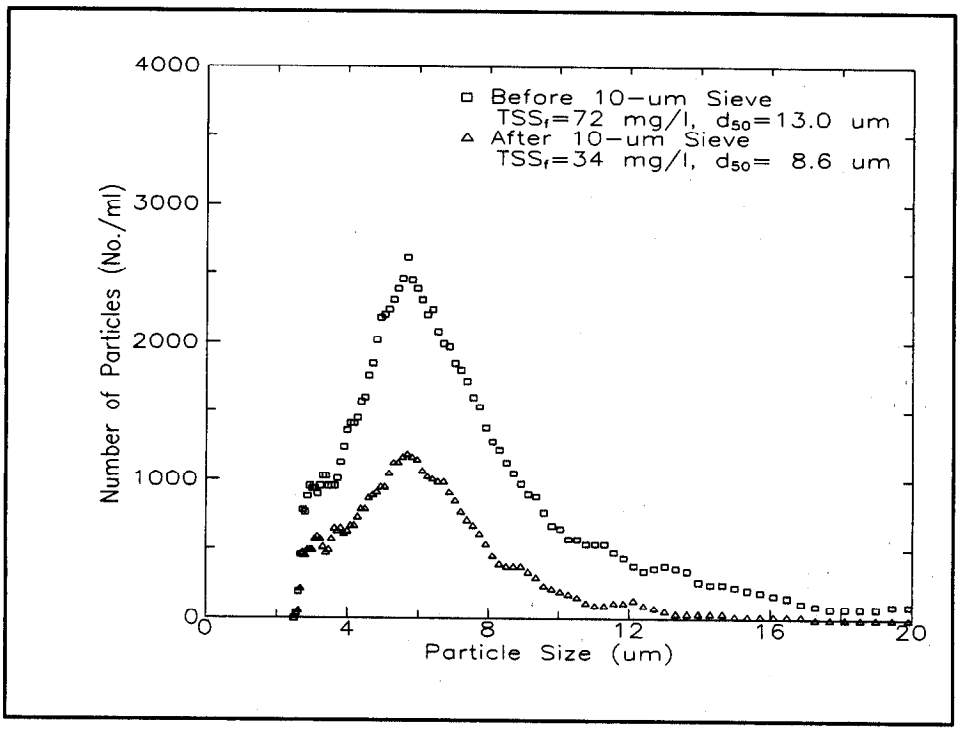


Figure 3. Number PSD for wet-sieved samples

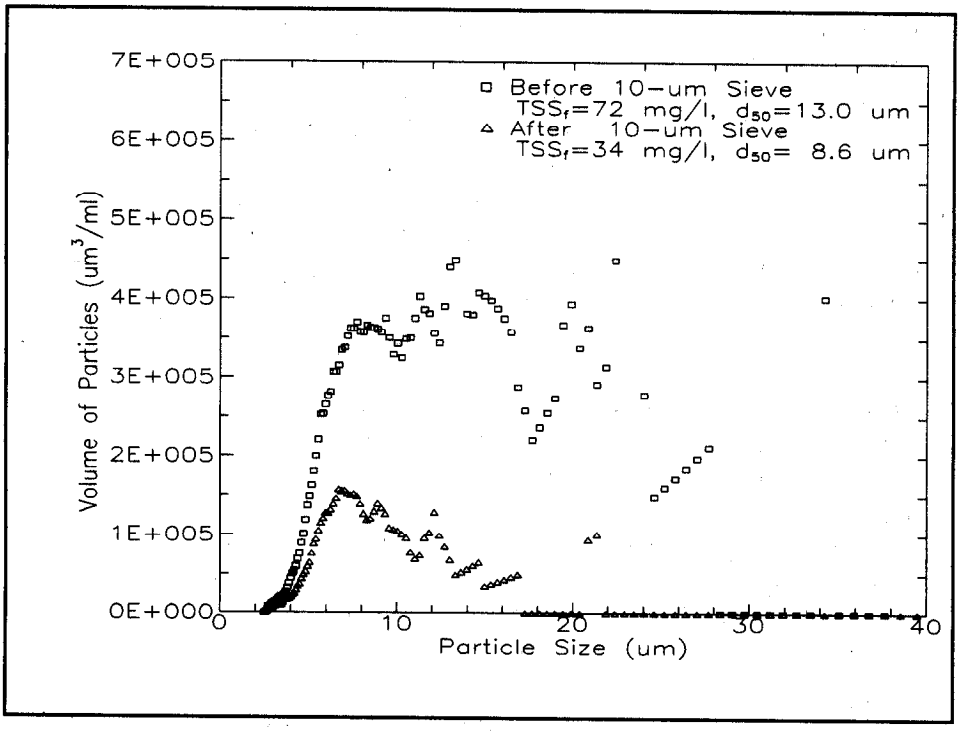


Figure 4. Volume PSD for wet-sieved samples

Table 9
Particle Characteristics Before and After Wet Sieving

Sample	Final TSS mg/ℓ	d_{50} μm	GSD	Surface Area mm^2/ml	Total PCB μg/ℓ	Sorbed PCB	
						μg/g	$\mu g/mm^2 \times 10^{-3}$
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.

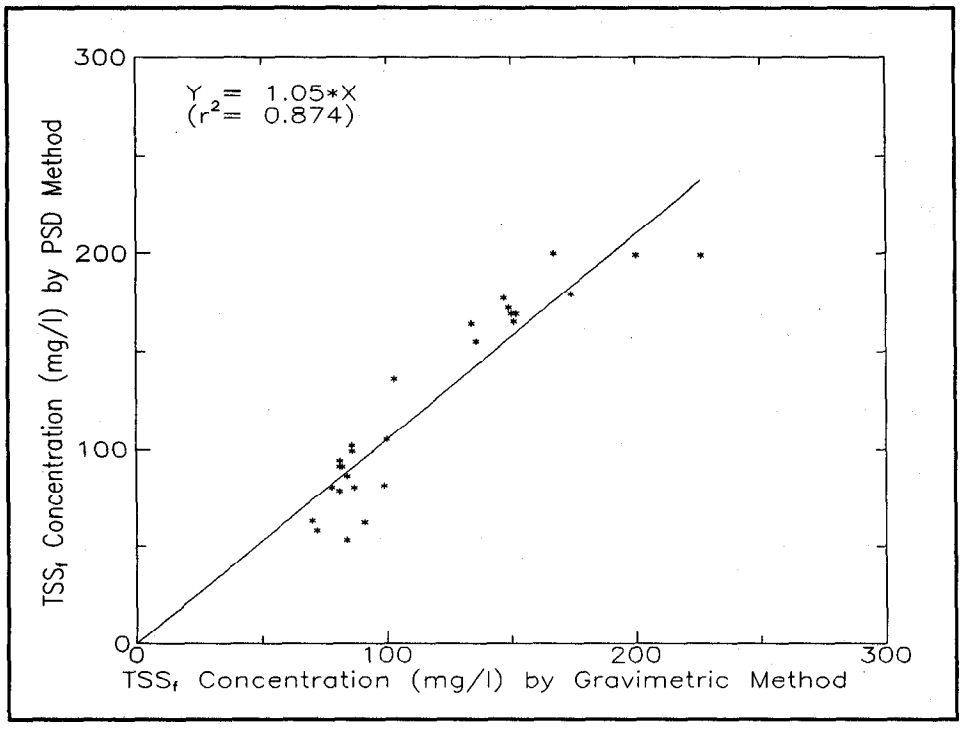


Figure 5. Comparison of TSS_f measured by gravimetric method to TSS_f measurement by PSD method

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:

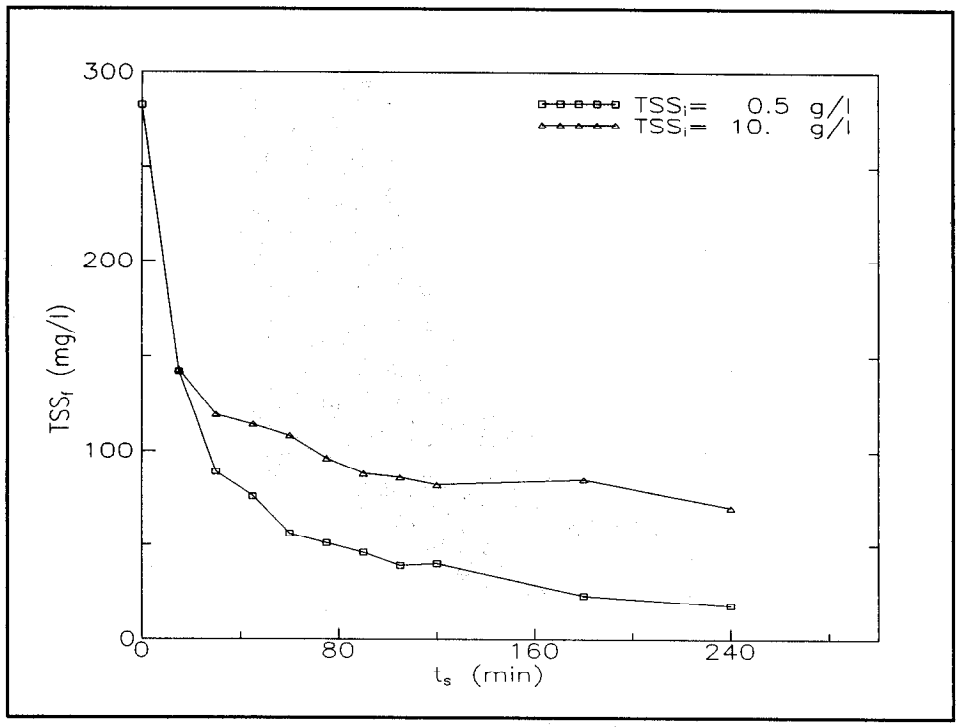


Figure 6. TSS_f as a function of time after a 1-hr aeration time

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

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

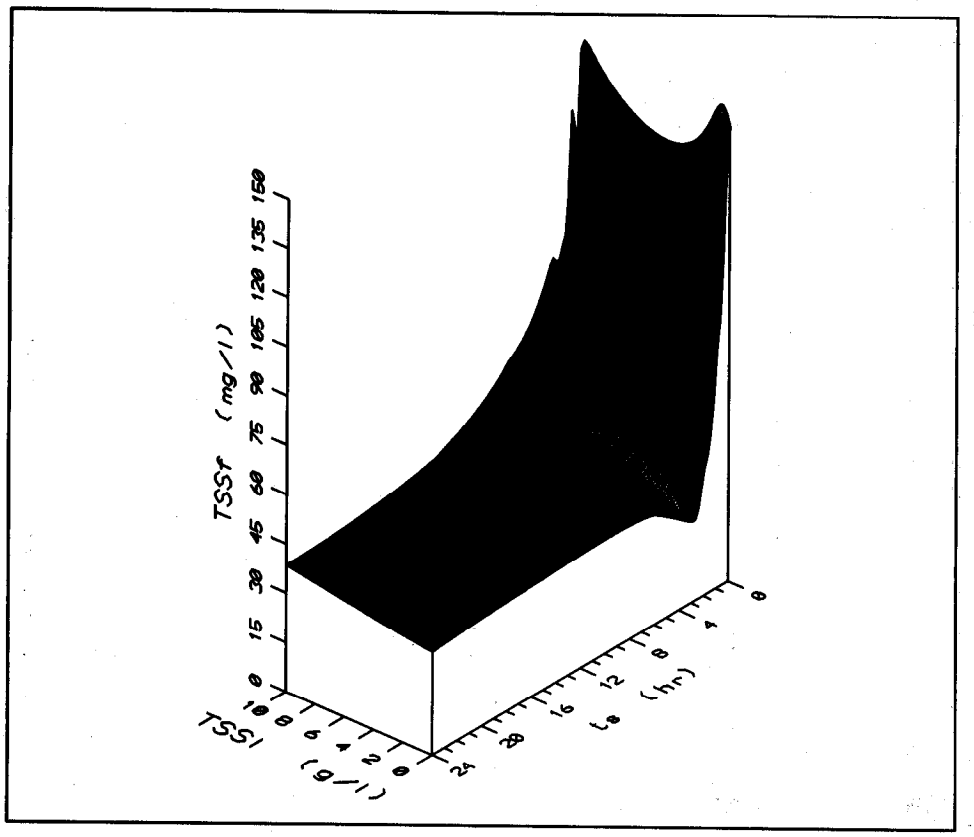


Figure 7. TSS_f surface as a function of settling time(t_s) and initial suspended solids concentration (TSS_i)

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

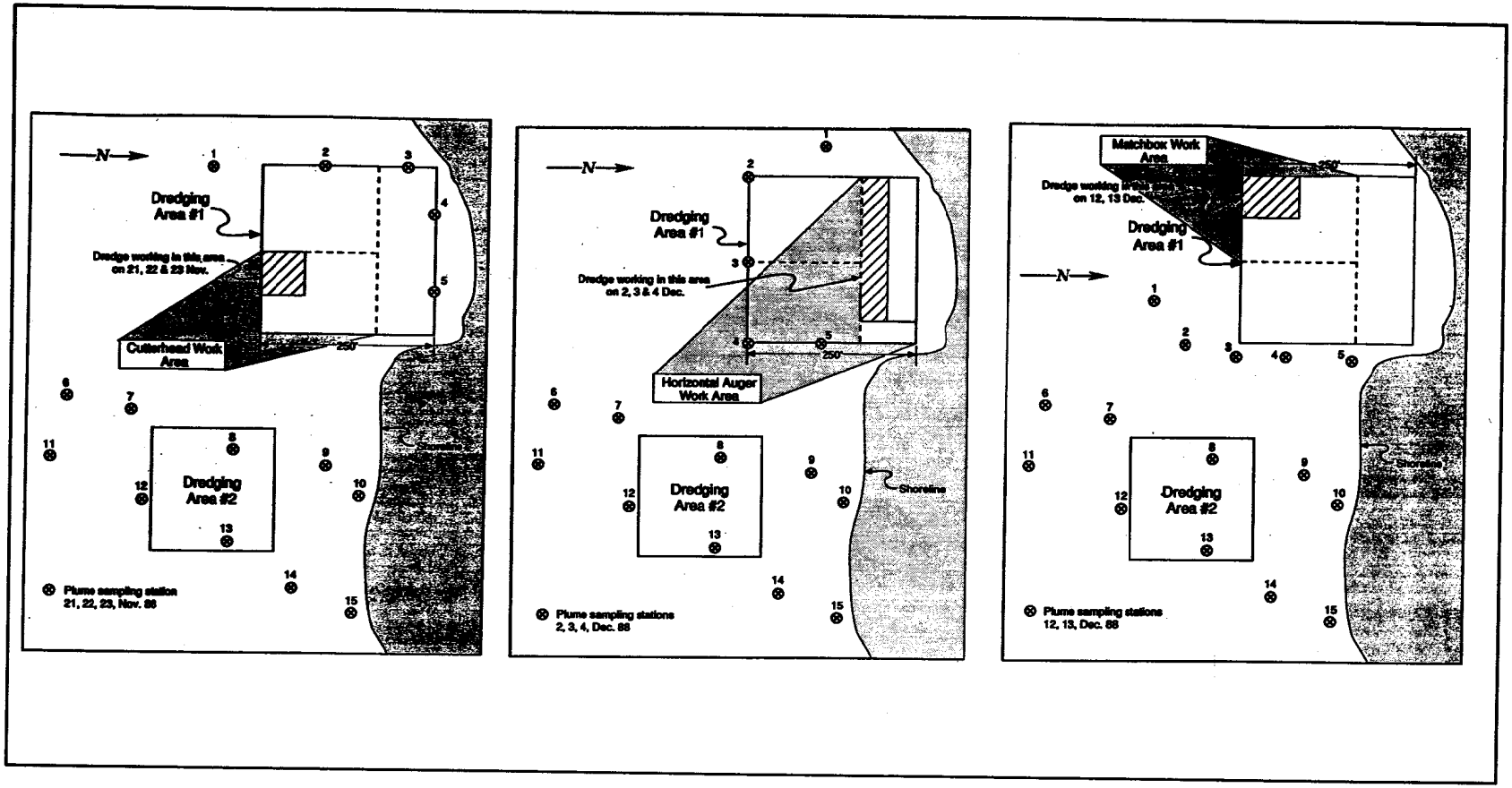


Figure 8. Field sample location map

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 predredged 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

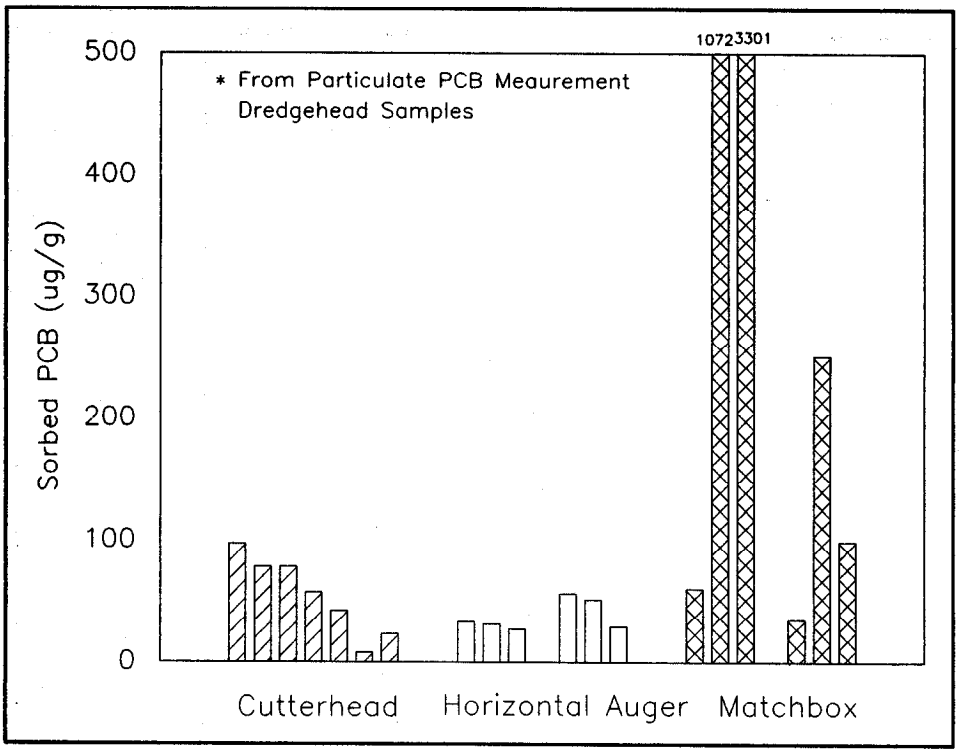


Figure 9. Comparison of sorbed PCB for dredgehead samples

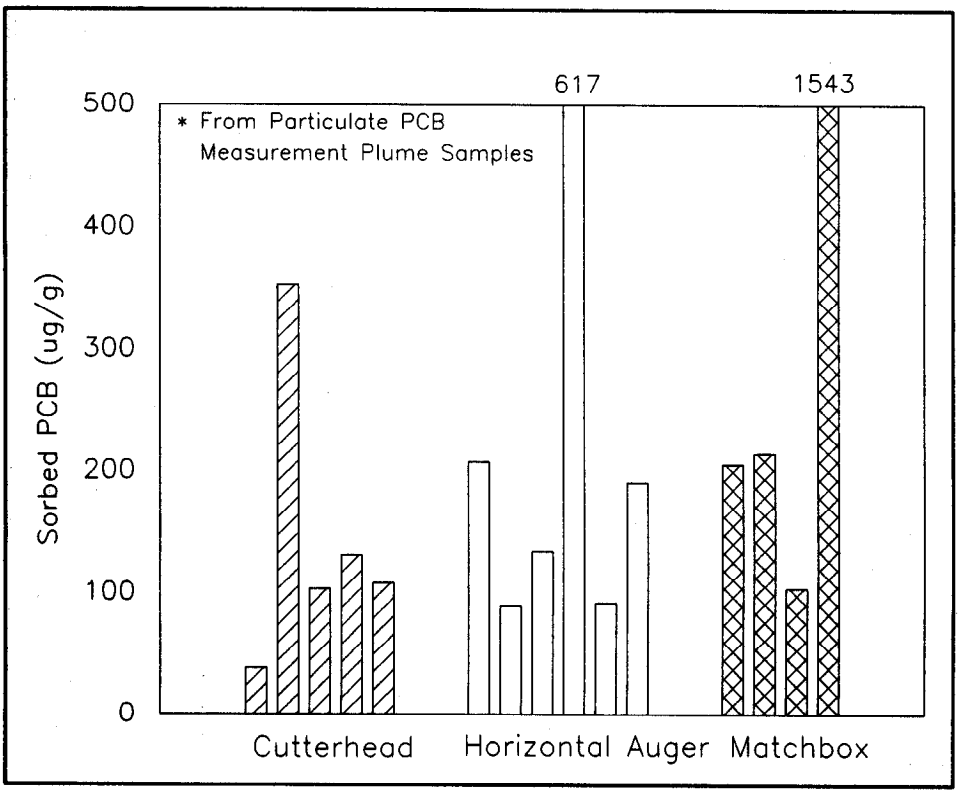


Figure 10. Comparison of sorbed PCB for plume samples

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

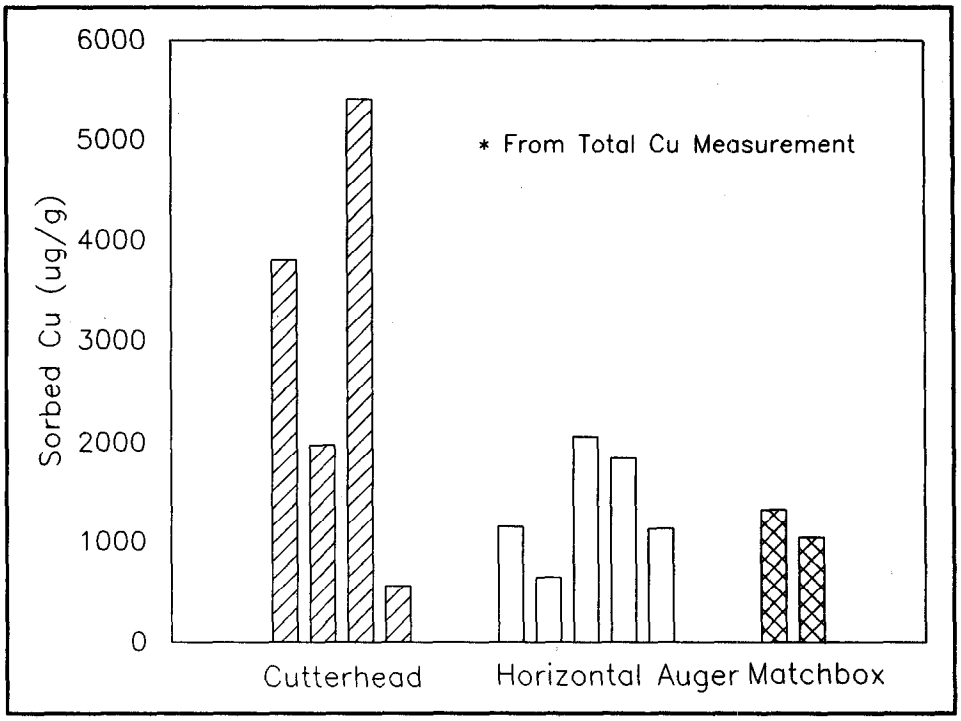


Figure 11. Sorbed Cu concentrations as a function of dredgehead type

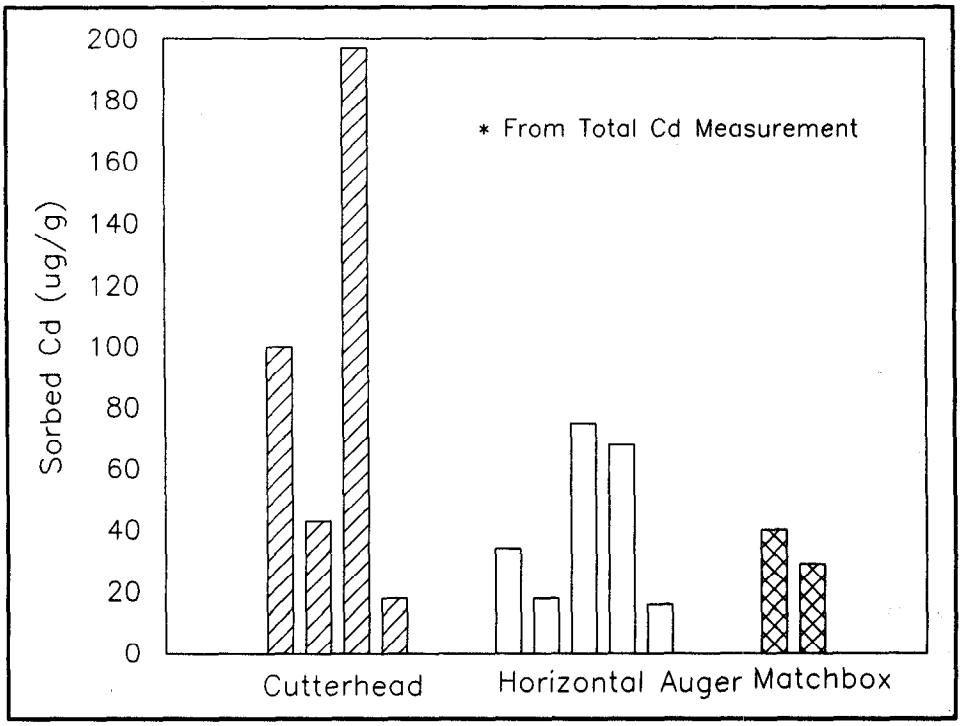


Figure 12. Sorbed Cd concentrations as a function of dredgehead type

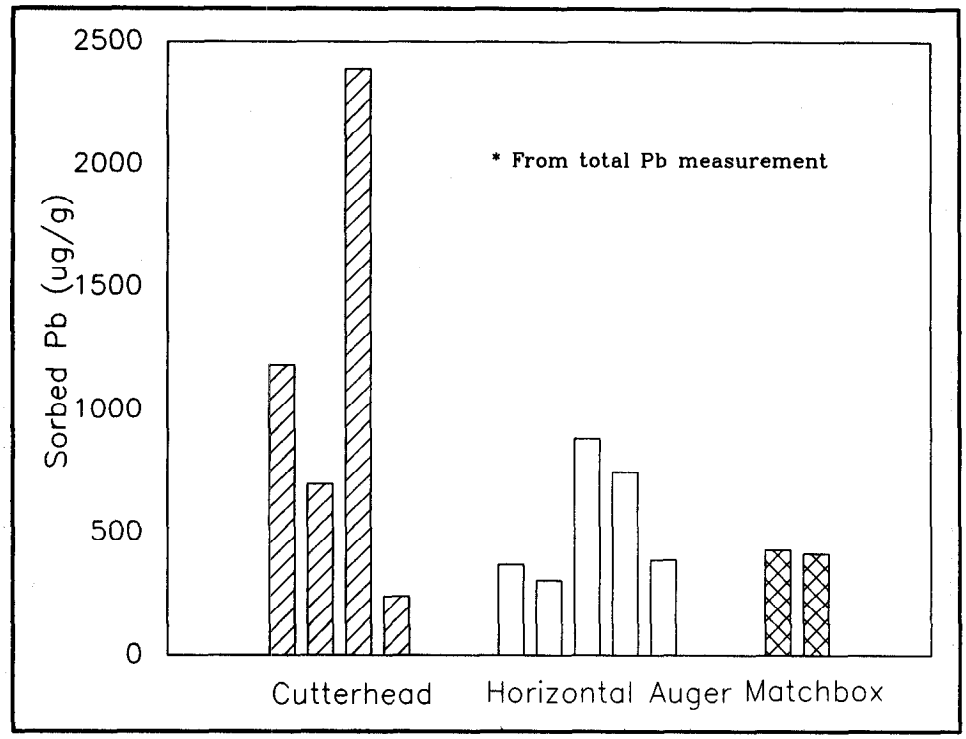


Figure 13. Sorbed Pb concentrations as a function of dredgehead type

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

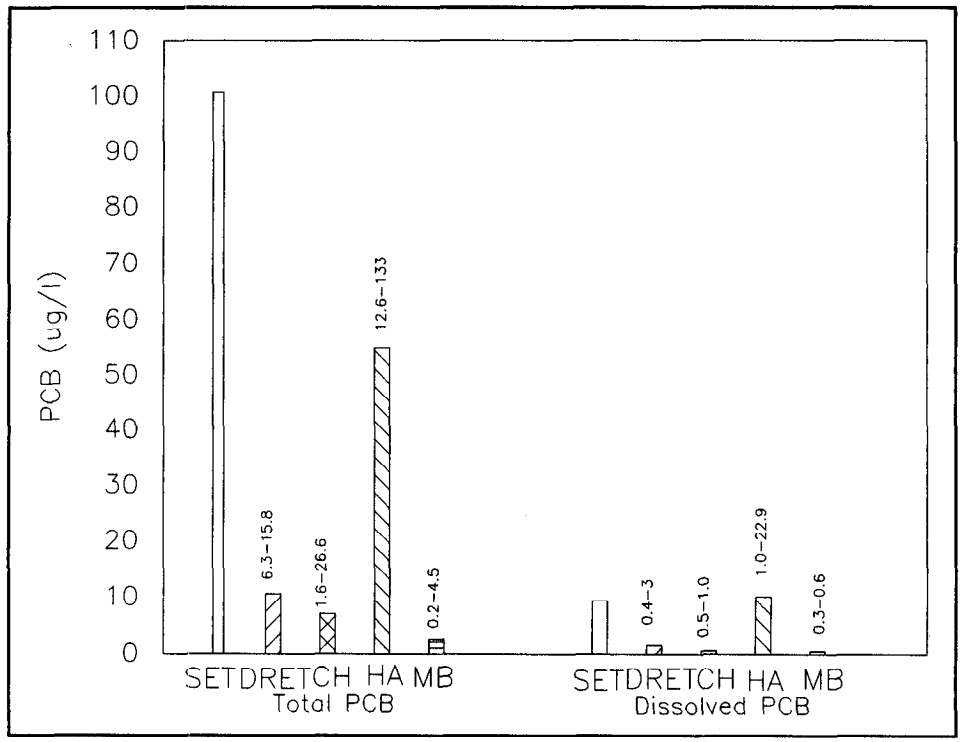


Figure 14. Comparison of PCB concentrations for field dredgehead samples (CH-cutterhead, HA-horizontal auger, MB-matchbox), DRET, and SET results

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

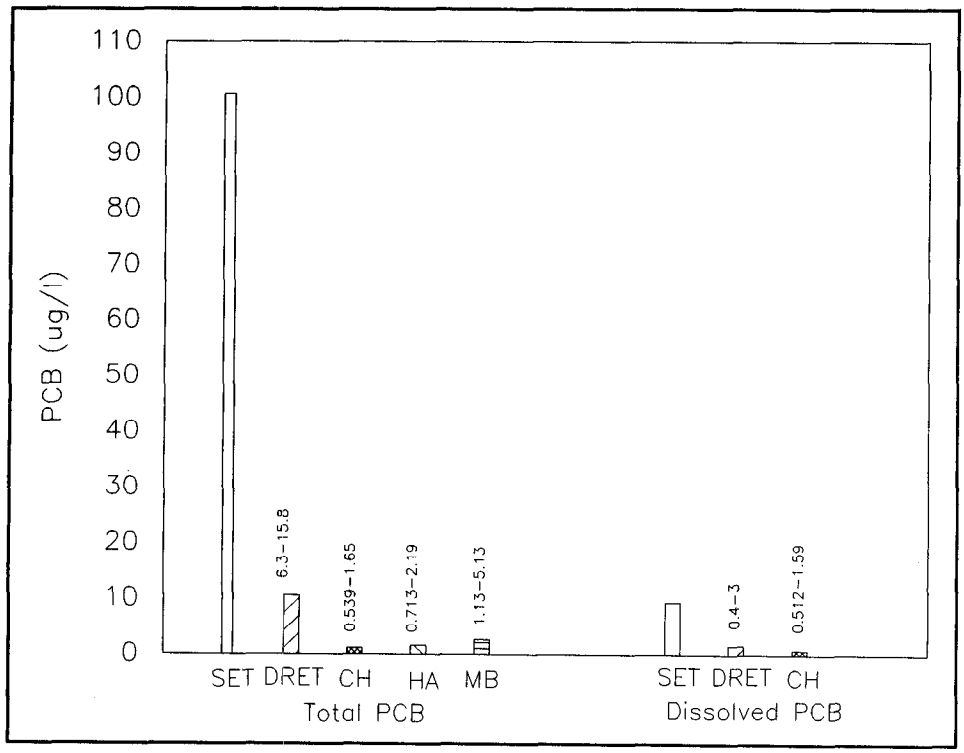


Figure 15. Comparison of PCB concentrations for field plume samples (CH-cutterhead, HA-horizontal auger, MB-matchbox), DRET, and SET results

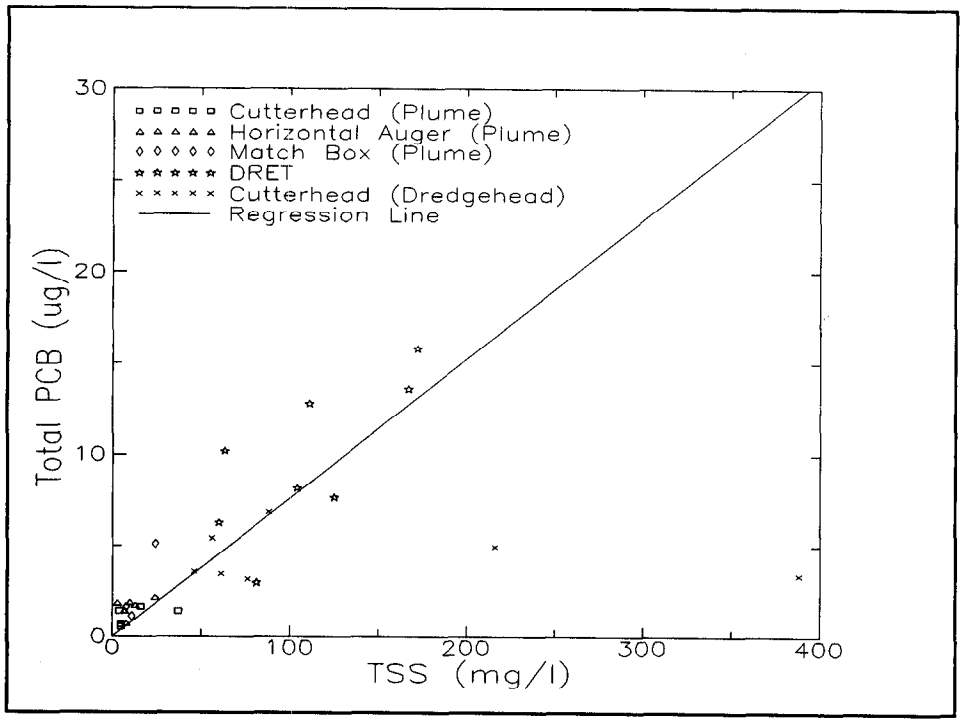


Figure 16. Relationship between total PCB and TSS concentrations

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

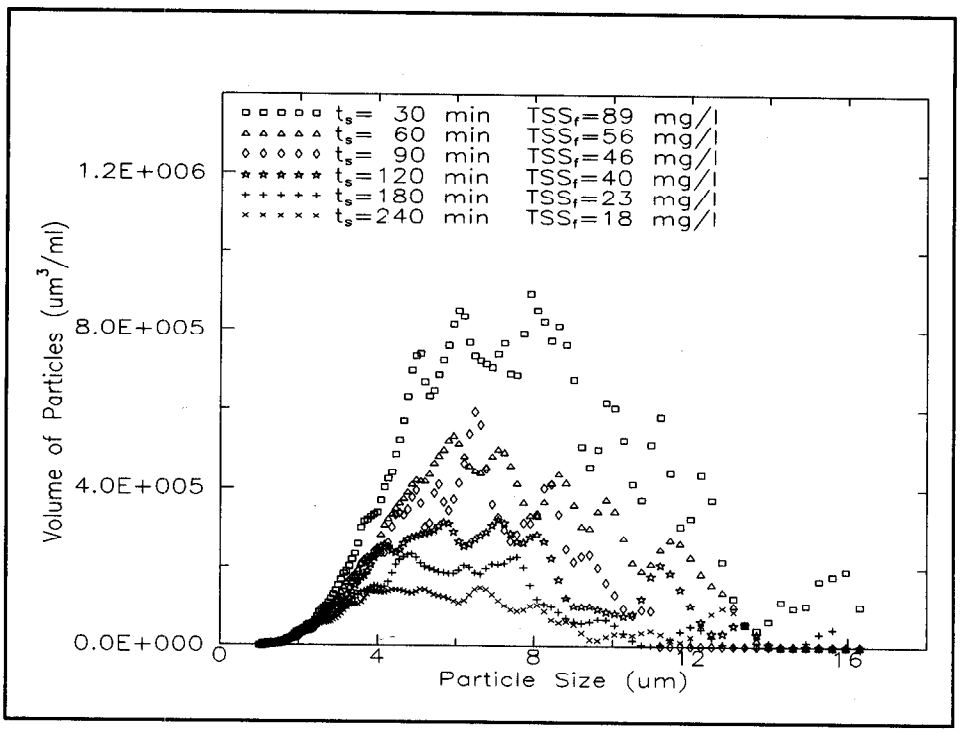


Figure 17. Volume PSD as a function of settling time

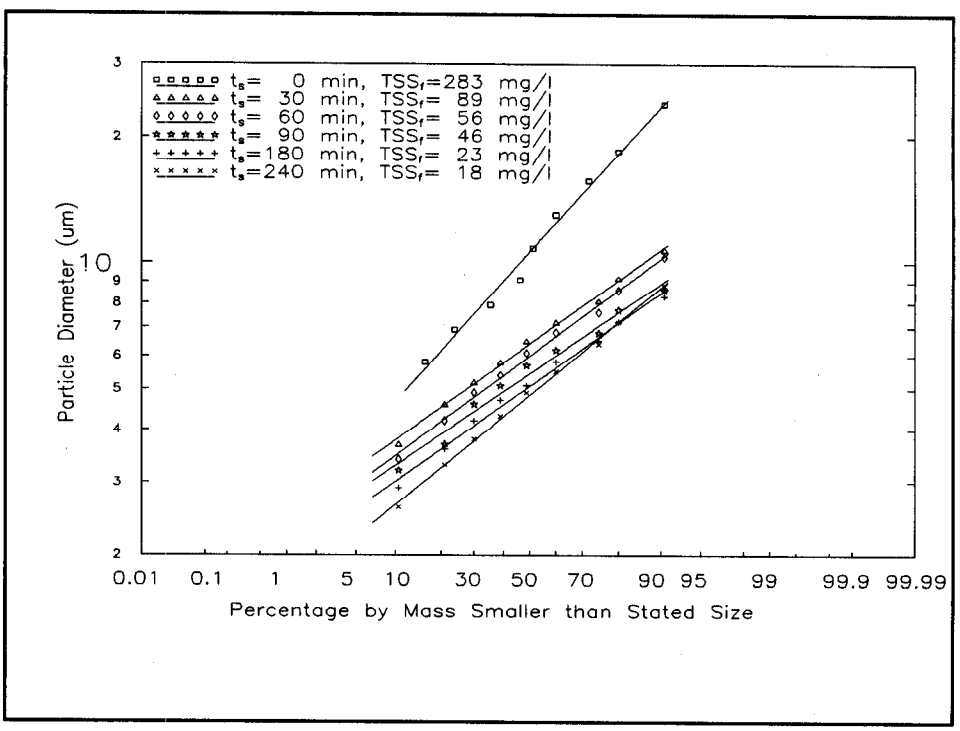


Figure 18. Log-normal PSD as a function of settling time

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

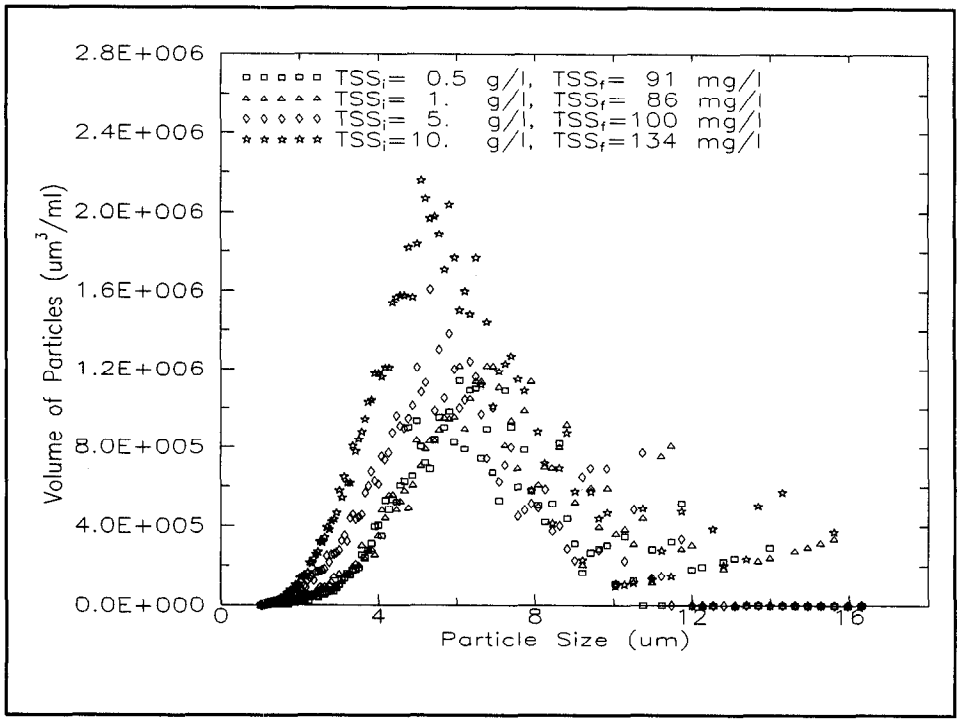


Figure 19. Volume PSD as function of TSS_i concentration

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.

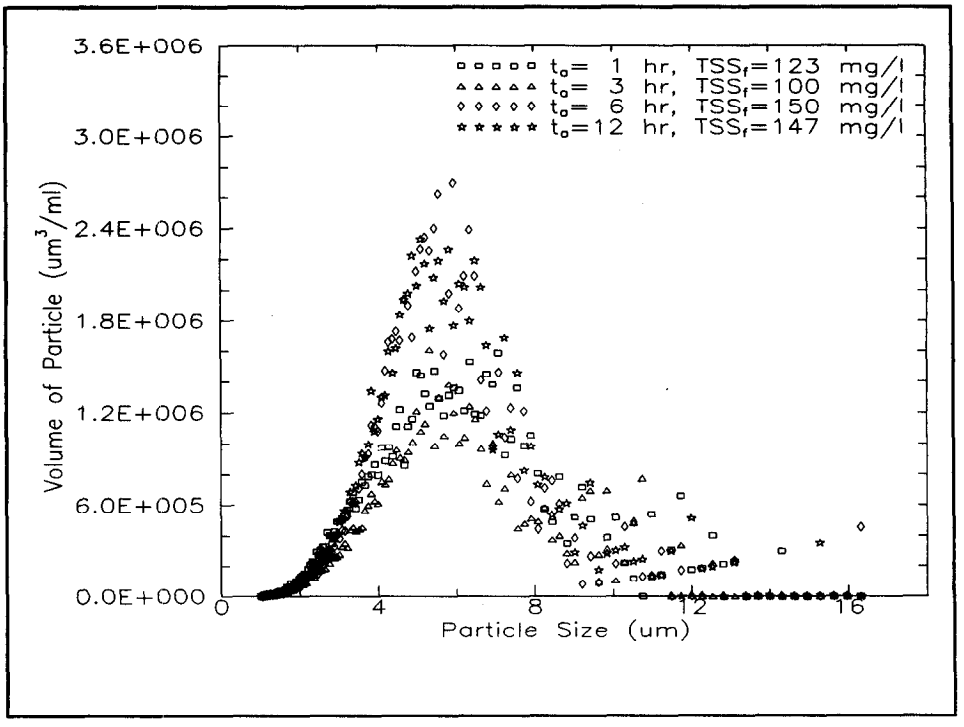


Figure 20. Volume PSD as a function of aeration time

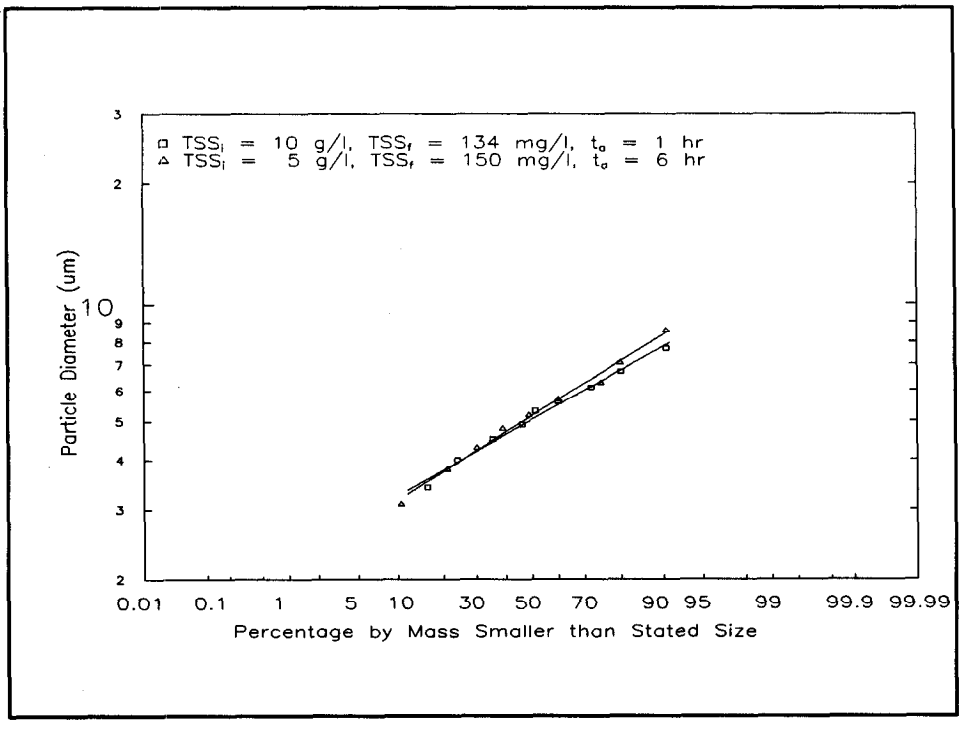


Figure 21. Log-normal PSD as a function of aeration and settling times

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:

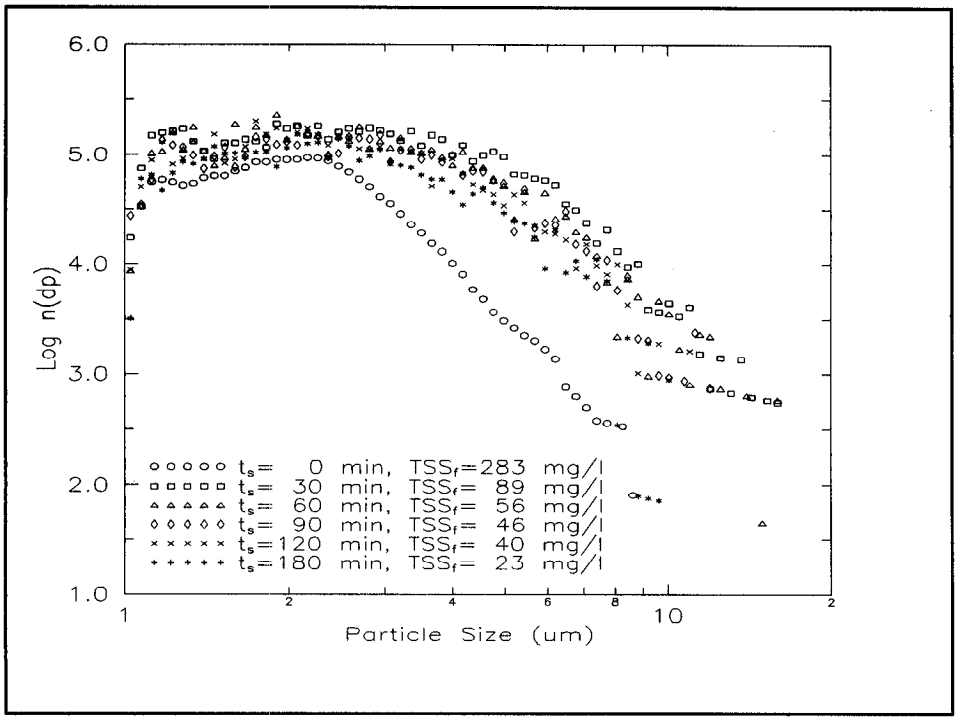


Figure 22. Log-normal PSD as a function of settling time

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.

$$v_s = \frac{20}{t} \text{ cm/min} \qquad (6)$$

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

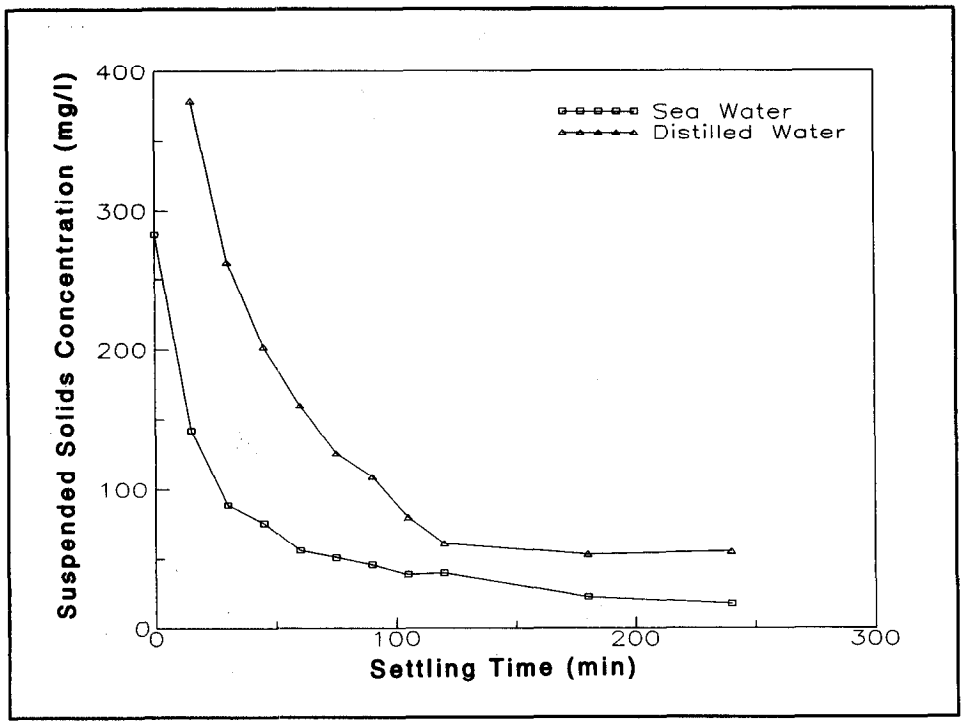


Figure 23. Settling behavior for TSS_i concentrations of 0.5 g/ℓ

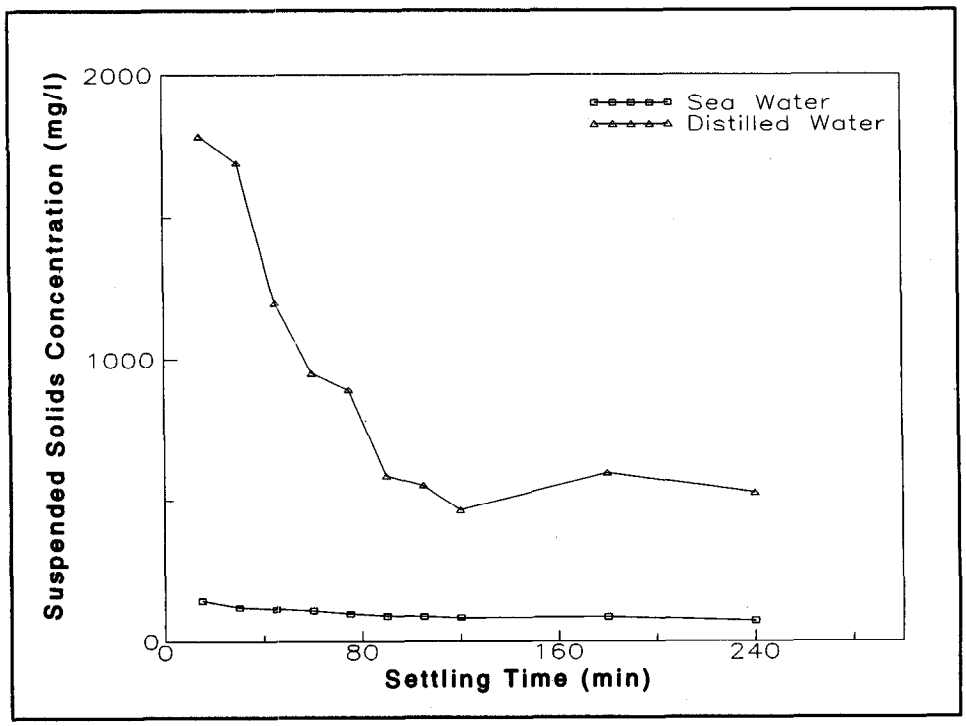


Figure 24. Settling behavior for TSS_i concentrations of 10 g/ℓ

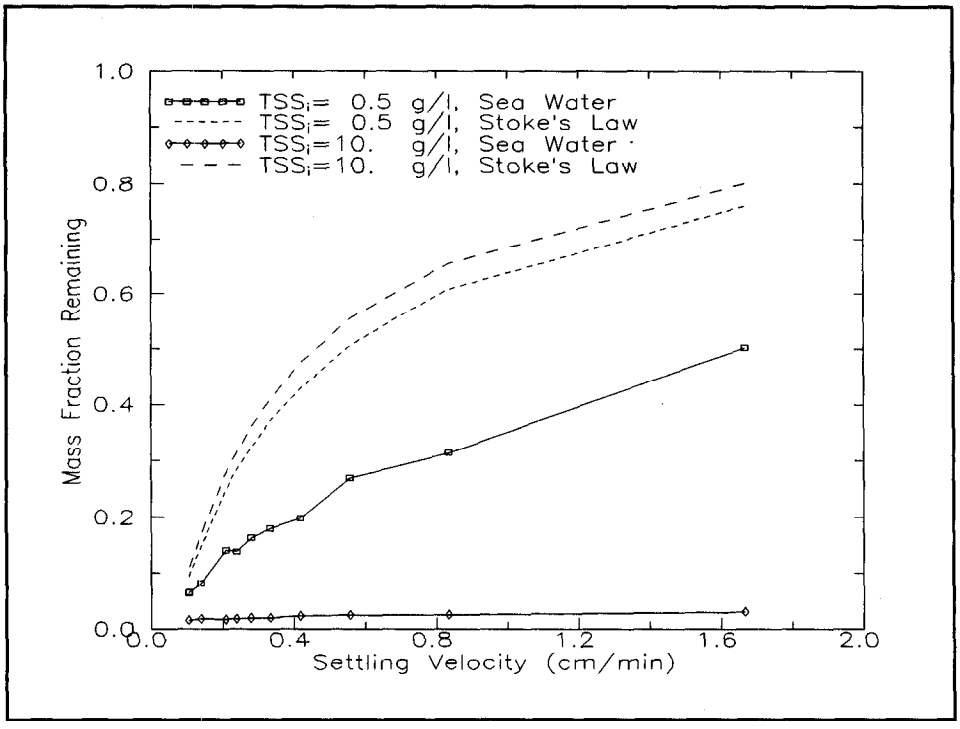


Figure 25. Comparison of observed settling characteristics and Stoke's law predictions

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:

$$M_s q_i = V_l C_e + M_s K_p C_e \quad (8)$$

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:

$$K_p = f_{oc} K_{oc} \quad (9)$$

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] 1242	% Composition[a] 1254	Log K_{ow}[b]
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

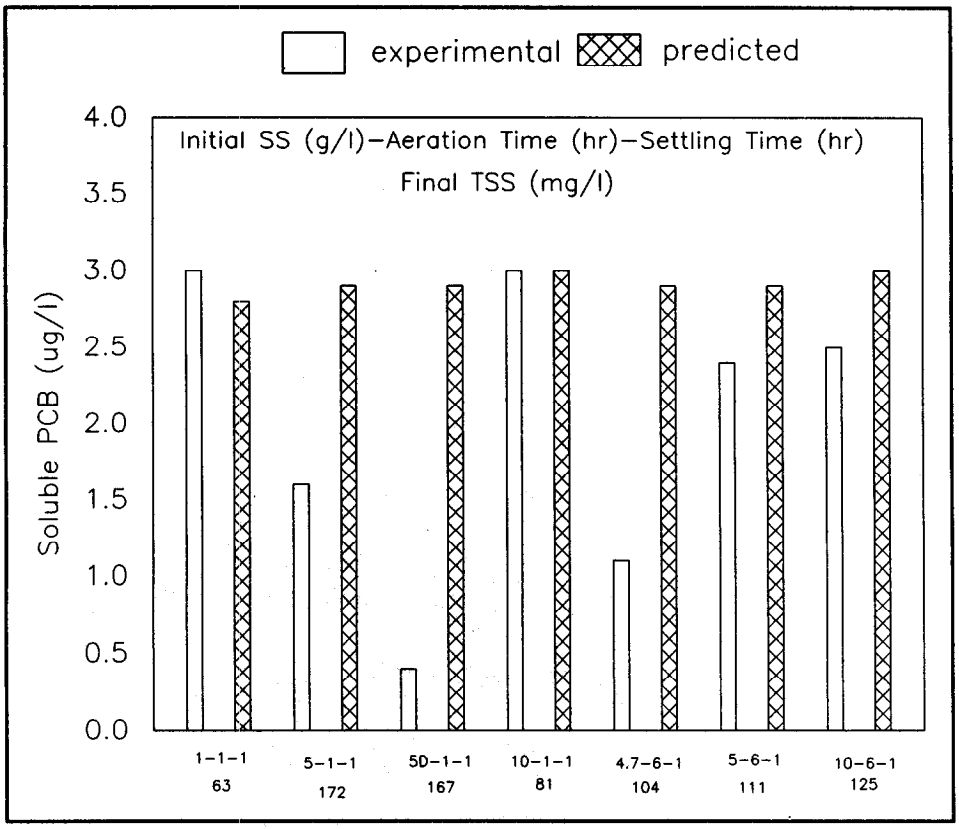


Figure 26. Comparison of measured and predicted soluble PCB concentrations

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).

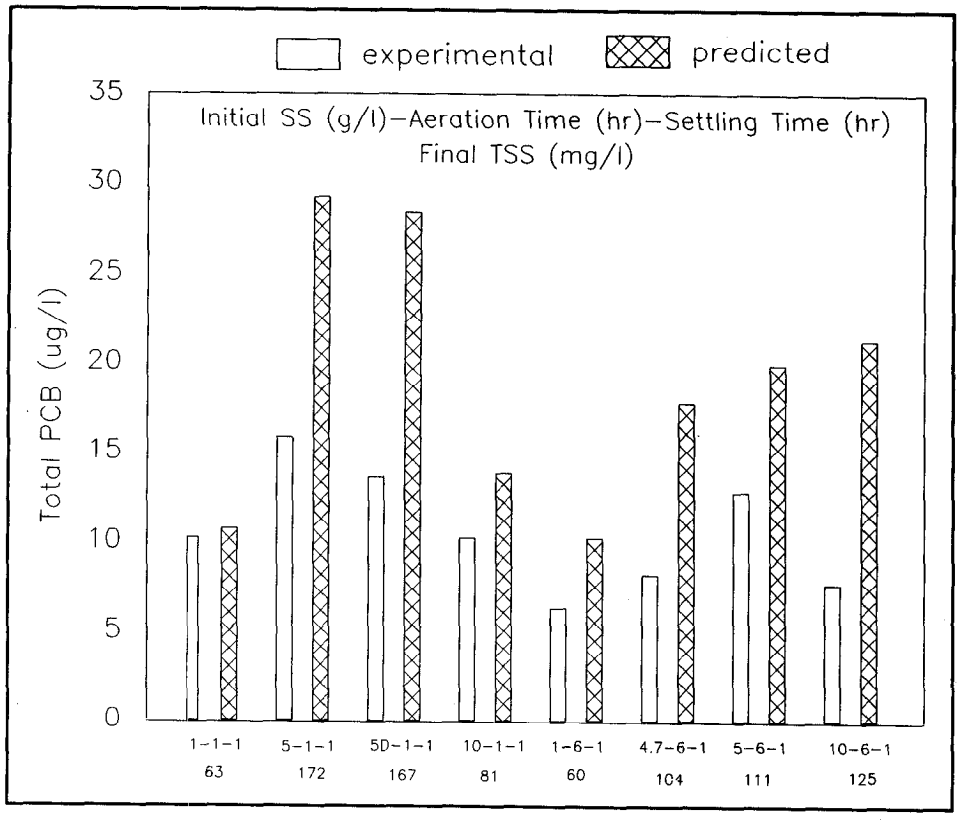


Figure 27. Comparison of measured and expected total PCB concentrations

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

---

[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.

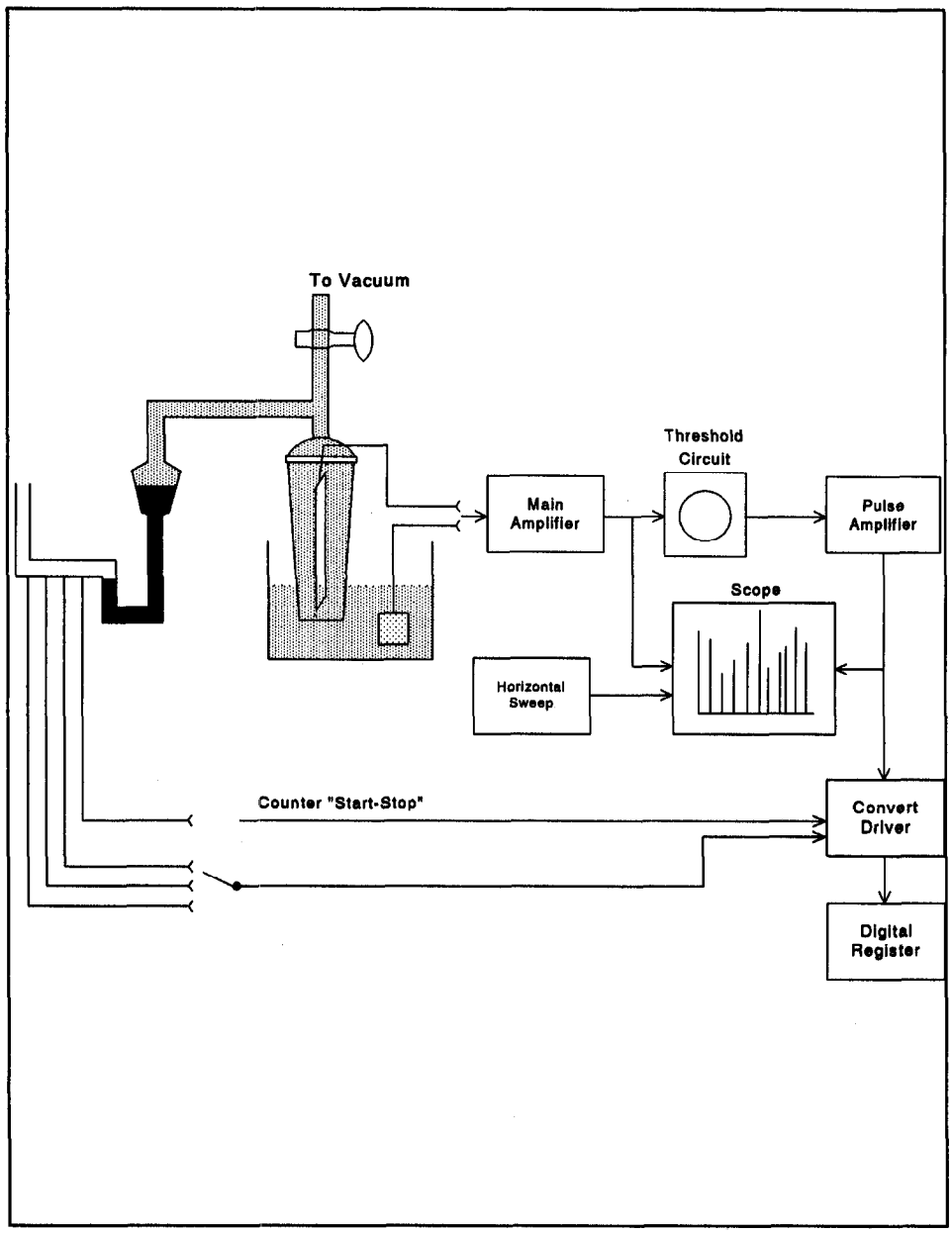


Figure A1. Schematic diagram of PSD analyzer

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	3. REPORT TYPE AND DATES COVERED
	August 1995	Final report

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

5. FUNDING NUMBERS

6. AUTHOR(S)
Francis A. DiGiano, Cass T. Miller, Jeyong Yoon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Environmental Sciences and Engineering
University of North Carolina
Chapel Hill, NC 27599

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	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED		

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

• U.S. GOVERNMENT PRINTING OFFICE: 1995-633-144/00022

Appendix 4

SOP – Paint Filter Liquids Test (SW-846 Method 9095A)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD 9095A

PAINT FILTER LIQUIDS TEST

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the presence of free liquids in a representative sample of waste.

1.2 The method is used to determine compliance with 40 CFR 264.314 and 265.314.

2.0 SUMMARY OF METHOD

2.1 A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5-min test period, the material is deemed to contain free liquids.

3.0 INTERFERENCES

3.1 Filter media were observed to separate from the filter cone on exposure to alkaline materials. This development causes no problem if the sample is not disturbed.

3.2 Temperature can affect the test results if the test is performed below the freezing point of any liquid in the sample. Tests must be performed above the freezing point and can, but are not required to, exceed room temperature of 25^{o} C.

4.0 APPARATUS AND MATERIALS

4.1 Conical paint filter: Mesh number 60 +/- 5% (fine meshed size). Available at local paint stores such as Sherwin-Williams and Glidden.

4.2 Glass funnel: If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least 1 in. of the filter mesh to protrude should be used to support the filter. The funnel should be fluted or have a large open mouth in order to support the paint filter yet not interfere with the movement, to the graduated cylinder, of the liquid that passes through the filter mesh.

4.3 Ring stand and ring, or tripod.

4.4 Graduated cylinder or beaker: 100-mL.

5.0 REAGENTS

5.1 None.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected according to the directions in Chapter Nine of this manual.

6.2 A 100-mL or 100-g representative sample is required for the test. If it is not possible to obtain a sample of 100 mL or 100 g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100 mL or 100 g, i.e., 200, 300, 400 mL or g. However, when larger samples are used, analysts shall divide the sample into 100-mL or 100-g portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids. If the sample is measured volumetrically, then it should lack major air spaces or voids.

7.0 PROCEDURE

7.1 Assemble test apparatus as shown in Figure 1.

7.2 Place sample in the filter. A funnel may be used to provide support for the paint filter. If the sample is of such light bulk density that it overflow the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter and above the mesh. Settling the sample into the paint filter may be facilitated by lightly tapping the side of the filter as it is being filled.

7.3 In order to assure uniformity and standardization of the test, material such as sorbent pads or pillows which do not conform to the shape of the paint filter, should be cut into small pieces and poured into the filter. Sample size reduction may be accomplished by cutting the sorbent material with scissors, shears, knife, or other such device so as to preserve as much of the original integrity of the sorbent fabric as possible. Sorbents enclosed in a fabric should be mixed with the resultant fabric pieces. The particles to be tested should be reduced smaller than 1 cm (i.e., should be capable of passing through a 9.5 mm (0.375 inch) standard sieve). Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce many "fine particles" which would normally not be present.

7.4 For brittle materials larger than 1 cm that do not conform to the filter, light crushing to reduce oversize particles is acceptable if it is not practical to cut the material. Materials such as clay, silica gel, and some polymers may fall into this category.

7.5 Allow sample to drain for 5 min into the graduated cylinder.

7.6 If any portion of the test material collects in the graduated cylinder in the 5-min period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

8.0 QUALITY CONTROL

8.1 Duplicate samples should be analyzed on a routine basis.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None provided.

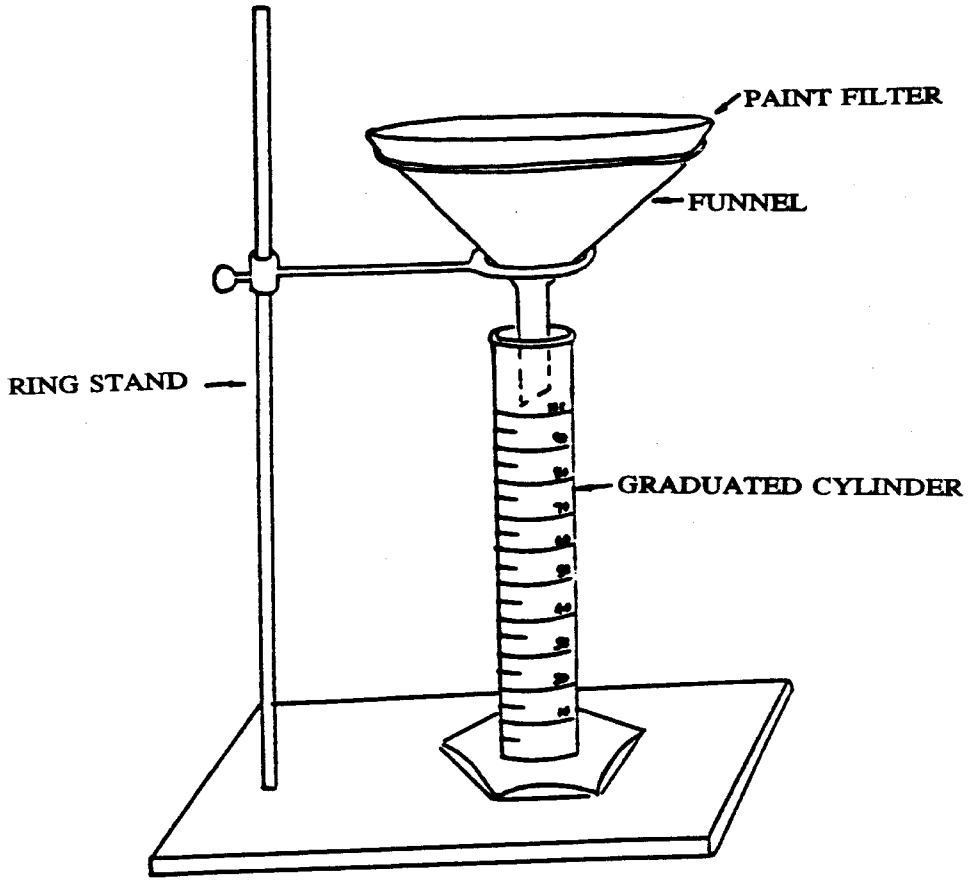
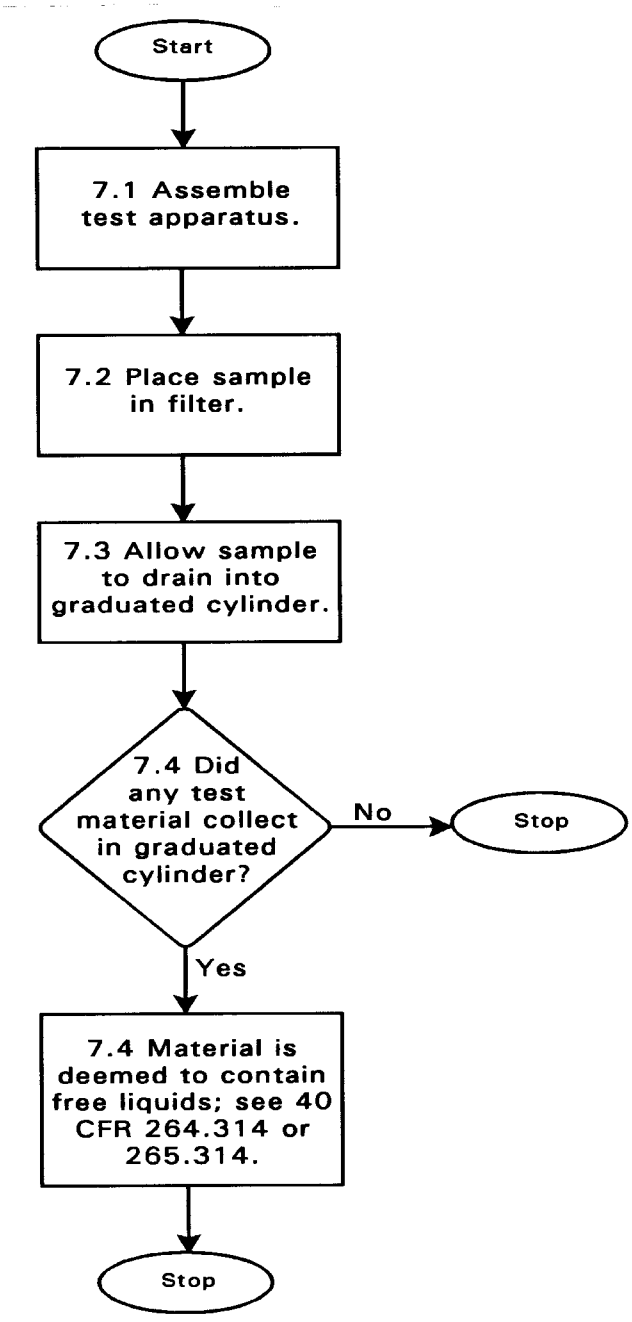


Figure 1. Paint filter test apparatus.


Start
7.1 Assemble test apparatus.
7.2 Place sample in filter.
7.3 Allow sample to drain into graduated cylinder.
7.4 Did any test material collect in graduated cylinder?
No
Stop
Yes
7.4 Material is deemed to contain free liquids; see 40 CFR 264.314 or 265.314.
Stop

Appendix 5

SOP – Stabilization/Solidification Testing (Andromelos & Ameel, 2003)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Stabilization/Solidification Tests

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for conducting bench scale Stabilization/Solidification Tests. Samples to be tested will include residuals produced from processes simulating various treatment operations for dredged material slurries from Hudson River sediments. These tests will determine the effectiveness of the treatment for landfilling of the tested material.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- Stainless Steel mixing bowl;
- Soil mixing apparatus;
- Sample containers (2- quart)
- Laboratory notebook.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Test Procedure for Stabilization/Solidification

The Stabilization/Solidification test method described below will be conducted in a laboratory bench scale setup using dredged material slurry samples approximately 1 Kg in weight. The tests will be conducted under 5 different S/S reagent percentages, 0, 5, 10, 15, and 20 % (w/w). Portland cement will be the reagent used for all sample compositions, with an additional lime reagent sample at the 10 % (w/w) composition. The sediment slurry or filter press cake samples will be blended with the appropriate weight of reagent by thorough mixing in the stainless steel bowl. Mixed samples will then be placed in 2-in. cube molds. All samples will undergo a three day curing period before testing is conducted. Testing will then be performed including but not limited to; PCBs, specific gravity, paint filter tests, unconfined compressive strength, RCRA metals tests, TCLPs, PAH, PCDD/PCDF, consolidation, and TOC. Results will be summarized and necessary changes will be made accordingly.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 6

SOP – Size Separation Testing

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Size Separation Testing

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for size separation testing. These tests are part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

Hydraulically-transported sediments may be treated for preliminary removal of coarse (>0.075 mm) particulates. Removal of coarse/dense materials relieves loading of solids to dewatering facilities. It also offers the possibility of beneficial use of sand and coarse particles.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- Materials and equipment as required for Sieve analysis (ASTM D422 – see Appendix 10 of the SSAP QAPP).

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Size Separation Testing Procedure

1. PCB Distribution by Grain Size or Density Fraction testing

After preparation of simulated dredged material slurries, select a quantity containing approximately 500 grams of solids. This would be about 2 liters of H1 slurries (mechanically dredged and hydraulically offloaded at 25 % [w/w] solids content) or about 10 liters of H2 slurries (hydraulically dredged and hydraulically offloaded at 5 % [w/w] solids content).

Apply slurries to screens, following procedures of ASTM D422. Collect and weigh each size fraction and measure volume of fine fraction slurry. After weighing each fraction, aliquots of each sediment fraction and fine fraction slurry should be submitted for analysis of PCB content by GEHR modified Method 8082 (see Appendix 5 of the SSAP QAPP). Specific grain size fractions to be collected and analyzed may be modified based on discussions with the selected treatability test vendor.

A separation based on density, using a high-density liquid method, will also be performed to separate the sediment slurry samples into three fractions. Since these methods, as applied to sediments, are proprietary in nature, the SOP for this test will be developed in cooperation with the selected treatability test vendors.

After receipt of analytical results, a mass balance shall be prepared, showing distribution of particle size masses, with associated distributions of PCB mass on the solids and in associated fine fraction slurry.

2. Preparation of Desanded test slurries

Some of the treatability tests will use desanded dredge slurry as feed material, while other test sequences use simulated dredge slurry without desanding. When desanded feed material is required, it will be developed by passing the required quantity of simulated dredge slurry across a #200 screen with 0.075 millimeter openings. This mesh size may be adjusted, based on results of the sieve analyses described above. Aliquots of coarse solids and slurry containing fines will be sampled for each test sequence. The weight of coarse solids will also be measured, permitting a mass balance of coarse and fine solids for each desanding sequence. PCBs should also be measured for each run producing coarse and fine fractions.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 7

SOP – Drainage Study of Coarse Fraction

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Drainage Study of Coarse Fraction

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for conducting a Drainage Study of Coarse Fraction for use in treatability studies, as described in the Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

During processing of Hudson River dredged material, larger-sized particulates may be separated from finer solids in desanding process equipment such as hydrocyclones or screens. The separated coarse particulates would be drained and further evaluated for non-TSCA (Subtitle D) disposal or for beneficial use. The purpose of this study is to estimate the water content of separated coarse media after gravity draining for a period of time.

Specific dredged slurry simulations to be treated for size separation testing are presented on Table 2 of the TS Work Plan. The coarse fraction from each of these tests will be further tested in the Drainage Study of Coarse Fraction tests.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (BBL, 2003);
- No. 200 standard sieves;
- Sampling spoon; and
- Laboratory notebook.

III. Health and Safety Considerations

Refer to the Revised HASP (BBL, 2003).

IV. Drainage Study of Coarse Fraction Procedure

In this test, samples of the coarse fractions separated during size separation testing are placed atop a screen and gravity drained for several days. The remaining procedures for conducting a drainage study of coarse fractions are as follows:

1. The dredged slurry simulations selected for size separation testing are shown on the lines for data quality objectives (DQO) 4b. (1) and 4c. (1) of Table 2 in the TS Work Plan. Retain approximately 1 liter of separated coarse fraction from each of these size separation tests.

2. Place each 1-liter sample in a conical configuration upon a No. 200 standard sieve. Also take a 25-gram sample of each sample for measurement of initial solids concentration.

3. Place each screen and sample in a non-drafty location, such as a laboratory hood with the fan turned off.

4. After drainage durations of approximately 24, 48, and 72 hours, remove one sample from the center of the cone and submit for solids concentrations.

For each coarse fraction sample, plot the solids concentration vs time.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 8

SOP – Standard Practice for Coagulation-Flocculation Jar Test (ASTM D2035)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Designation: D 2035 – 80 (Reapproved 1995)ε1

Standard Practice for Coagulation-Flocculation Jar Test of Water[1]

This standard is issued under the fixed designation D 2035; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε1 NOTE—Section 12 was added editorially in December 1994.

1. Scope

1.1 This practice covers a general procedure for the evaluation of a treatment to reduce dissolved, suspended, colloidal, and nonsettleable matter from water by chemical coagulation-flocculation, followed by gravity settling. The procedure may be used to evaluate color, turbidity, and hardness reduction.

1.2 The practice provides a systematic evaluation of the variables normally encountered in the coagulation-flocculation process.

1.3 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam[2]

D 1193 Specification for Reagent Water[2]

D 1293 Test Methods for pH of Water[2]

D 1889 Test Method for Turbidity of Water[2]

D 3370 Practices for Sampling Water[2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D 1129.

4. Summary of Practice

4.1 The coagulation-flocculation test is carried out to determine the chemicals, dosages, and conditions required to achieve optimum results. The primary variables to be investigated using the recommended practice include, but are not limited to:

4.1.1 Chemical additives,

4.1.2 pH,

4.1.3 Temperature, and

4.1.4 Order of addition and mixing conditions.

5. Significance and Use

5.1 This practice permits the evaluation of various coagulants and coagulant aids used in the treatment of water and waste water for the same water and the same experimental conditions.

5.2 The effects of concentration of the coagulants and coagulant aids and their order of addition can also be evaluated by this practice.

6. Interferences

6.1 There are some possible interferences that may make the determination of optimum jar test conditions difficult. These include the following:

6.1.1 *Temperature Change (During Test)*—Thermal or convection currents may occur, interfering with the settling of coagulated particles. This can be prevented by temperature control.

6.1.2 *Gas Release (During Test)*—Flotation of coagulated floc may occur due to gas bubble formation caused by mechanical agitator, temperature increase or chemical reaction.

6.1.3 *Testing-Period*—Biological activity or other factors may alter the coagulation characteristics of water upon prolonged standing. For this reason the period between sampling and testing should be kept to a minimum, with the time being recorded.

7. Apparatus

7.1 *Multiple Stirrer*—A multiposition stirrer with continuous speed variation from about 20 to 150 rpm should be used. The stirring paddles should be of light gage corrosion-resistant material all of the same configuration and size. An illuminated base is useful to observe the floc formation. Precautionary measures should be taken to avoid heat being imparted by the illumination system which may counteract normal settling.

7.2 *Jars (or Beakers)*, all of the same size and shape; 1500-mL Griffin beakers may be used (1000-mL recommended minimum size).

7.3 *Reagent Racks*—A means of introducing each test solution to all jars simultaneously. There should be at least one rack for each test solution or suspension. The racks should be similar to that shown in Fig. 1.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chem-

[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, and Surveillance of Water.

Current edition approved July 3, 1980. Published October 1980. Originally published as D 2035 – 64 T. Last previous edition D 2035 – 74.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

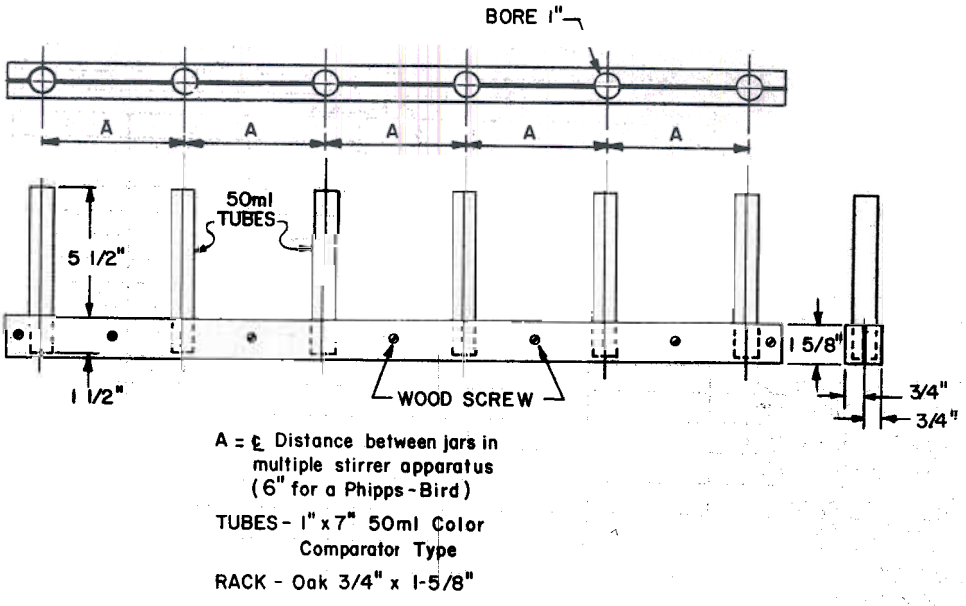


FIG. 1 Reagent Rack for Multiple Stirrer Jar Test Apparatus

ical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water for reagent preparation shall be understood to mean Type IV reagent water conforming to Specification D 1193.

8.3 The following chemicals and additives are typical of those used for test solutions and suspensions. The latter, with the exception of coagulant aids, may be prepared daily by mixing chemicals with water to a concentration of 10 (±0.1) g/L (1.0 mL of test solution or suspension when added to 1 L of sample is equivalent to 10 mg/L):

Prime Coagulants
- Alum[$Al_2(SO_4)_3 \cdot 18H_2O$]
- Ferric sulfate [$Fe_2(SO_4)_3 \cdot xH_2O$]
- Ferric chloride ($FeCl_3 \cdot 6H_2O$)
- Ferrous sulfate ($FeSO_4 \cdot 7H_2O$)
- Magnesium carbonate ($MgCO_3 \cdot 3H_2O$)
- Sodium aluminate ($NaAlO_2$)

Coagulant Aids
- Activated silica
- Anionic } Polyelectrolytes
- Cationic } Polyelectrolytes
- Nonionic Polymer

Oxidizing Agents
- Chlorine (Cl_2)
- Chlorine dioxide (ClO_2)
- Potassium permanganate ($KMnO_4$)
- Calcium hypochlorite [$CaCl(ClO) \cdot 4H_2O$]
- Sodium hypochlorite (NaClO)

Alkalis
- Calcium carbonate ($CaCO_3$)
- Dolomitic lime (58 % CaO, 40 % MgO)
- Lime, hydrated [$Ca(OH)_2$]
- Magnesium oxide (MgO)
- Sodium carbonate (Na_2CO_3)
- Sodium hydroxide (NaOH)

Weighting Agents
- Bentonite
- Kaolin
- Other clays and minerals

Miscellaneous
- Activated carbon (powdered)

8.4 *Coagulant Aids*—There are numerous commercially available coagulant aids or polyelectrolytes. All polyelectrolytes are classified anionic, cationic or nonionic, depending upon their composition. These aids may have the ability to produce large, tough, easily-settled floc when used alone or in conjunction with inorganic coagulants. A small dosage (under 1 mg/L) may permit a reduction in the dosage of, or complete elimination of, the coagulant. In the latter case, the polyelectrolyte would be considered the prime coagulant rather than a coagulant aid. Aids come in powdered and liquid form. Powdered aids should be prepared as 0.1 % solutions with appropriate aliquots to provide proper dosage. Always add powdered aids to the dissolving water rather than the reverse, and add slowly to the shoulder of a vortex created by stirring. If a vortex is not formed, the dry powder will merely collect on the surface of the water in gummy masses and become very difficult to dissolve. Dissolving time may vary from several minutes to several hours. Suggested manufacturers' procedures for wetting, dissolving, and storing should be followed when available. Liquid forms can be readily prepared to the above strength without difficulty.[4]

9. Sampling

9.1 Collect the water sample under test in accordance with the applicable Specification D 1192 and Practices D 3370.

10. Procedure

10.1 Measure equal volumes (1000 mL) of sample into

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[4] A periodically updated "Report on Coagulant Aids for Water Treatment" is published by the Environmental Protection Agency Office of Water Supply, Cincinnati, Ohio 45268, listing coagulant aids that may be used in water treatment without adverse physiological effects on those using the water, based on information submitted by the manufacturers or distributors, or both.

Sample_____ pH _____ Turbidity_____ Date _____

Location_____ Color_____ Temperature_____ Sample Size_____ ml

	JAR NUMBER					
	1	2	3	4	5	6
Chemicals, mg/litre *(a)*						
Flash Mix Speed, rpm						
Flash Mix Time, min						
Slow Mix Speed, rpm						
Slow Mix Time, min						
Temperature, °F						
Time First Floc, min						
Turbidity						
pH						

(a) Indicate order of addition of chemicals

FIG. 2 Jar Test Data

each of the jars or 1500-mL Griffin beakers. As many sample portions may be used as there are positions on the multiple stirrer. Locate beakers so that the paddles are off-center, but clear the beaker wall by about 6.4 mm (¼ in.). Record the sample temperature at the start of the test.

10.2 Load the test chemicals in the reagent racks. Use one rack for each series of chemical additions. Make up each tube in the rack to a final volume of 10 mL, with water, before using. There may be a situation where a larger volume of reagent will be required. Should this condition prevail, fill all tubes with water to a volume equal to the largest volume of reagent in the reagent rack. When adding slurries, it may be necessary to shake the rack to produce a swirling motion just prior to transfer.

10.3 Start the multiple stirrer operating at the "flash mix" speed of approximately 120 rpm. Add the test solution or suspensions, at predetermined dosage levels and sequence. Flash mix for approximately 1 min after the additions of chemicals. Record the flash mix time and speed (rpm).

10.4 Reduce the speed as necessary to the minimum required to keep floc particles uniformly suspended throughout the "slow mix" period. Slow mix for 20 min. Record the time for the first visible floc formation. Every 5 min (during the slow mix period), record relative floc size and mixer speed (rpm). If coagulant aids are used, mixing speed is critical because excessive stirring tends to break up early floc formation and may redisperse the aid.

10.5 After the slow mix period, withdraw the paddles and observe settling of floc particles. Record the time required for the bulk of the particles to settle. In most cases this time will be that required for the particles to settle to the bottom of the beaker; however, in some cases there may be interfering convection currents. If so, the recorded settling time should be that at which the unsettled or residual particles appear to be moving equally upward and downward.

10.6 After 15 min of settling, record the appearance of floc on the beaker bottom. Record the sample temperature. By means of a pipet or siphon, withdraw an adequate sample volume of supernatant liquor from the jar at a point one half of the depth of the sample, to conduct color,[5] turbidity, pH and other required analyses, (Note) determined in accordance with Test Methods D 1889 and D 1293. A suggested form for recording results is appended (see Fig. 2).

NOTE—Tests for residual chemicals should be included, for example, alum; residual Al_2O_3; copperas; residual Fe_2O_3; etc.

10.7 Repeat steps 10.1 through 10.6 until all pertinent variables have been evaluated.

10.8 The times given in 10.3, 10.4, and 10.6 are only suggestions.

11. Reproducibility

11.1 It is recognized that reproducibility of results is important. To demonstrate reproducibility, the so-called 3 and 3 procedure is suggested. In this procedure, duplicate sets of 3 jars each are treated simultaneously with the same chemical dosages in jars 1 and 4, 2 and 5, and 3 and 6.

12. Keywords

12.1 coagulation; flocculation; jar tests

[5] For the color determination, reference is made to *Standard Methods for the Examination of Water and Waste Water*, Fourteenth edition, American Public Health Association, Inc., New York, NY, 1975, pp. 64–71.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

Appendix 9

SOP – Determine Optimum Polymer Dose

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Determine Optimum Polymer Dose

I. Scope and Application

This standard operating procedure (SOP) describes the procedure for determining optimum polymer dosage for sediment dewatering by plotting filtrate volumes vs. dosage from Buchner funnel or bench-scale filter press tests. These tests are part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

Hudson River dredged materials may be transported hydraulically to land-based processing facilities. Following desanding (particle size separation) the slurry of finer particulates will be dewatered, likely using a plate-and-frame filter press, belt press, or centrifuge. Chemical conditioning is required to facilitate water separation and obtain a dry cake which may be landfilled. Historically, conditioning has been obtained with inorganic materials, such as ferric chloride and lime, aluminum sulfate, and other multivalent cations. Today organic polyelectrolytes (or polymers) are typically used in dewatering and coagulation processes. Buchner funnel tests are a quick inexpensive method to monitor polymer dosage requirements or compare relative performance and cost of alternative chemical treatments.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- Graph paper or software.
- Applicable filtration equipment (to be specified by treatability laboratory).
- Laboratory notebook.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Determine Optimum Polymer Dose Procedure

Polymers (and inorganic coagulants) typically exhibit an optimum dosage. Below the optimum, performance increases with increasing dosage. Near the optimum there may be a "plateau" where performance stays the same with increasing dosage, but beyond the optimum, performance falls off with increasing dosage.

Buchner funnel or bench scale filter press tests can be used to find the optimum dosage for dewatering.

1. Typically, four dosages can be used to find the optimum, if those dosages are below and above the optimum.

2. Using the polymer solution concentration and the solids content of the dredge slurry material, each dosage in the bench scale test can be expressed as mg polymer per g of dry solids. For each dosage, test

performance can be measured as time to generate 100 cc of filtrate from a 200 cc treated sample. Alternately, test performance can be measured as cc filtrate released in a pre-determined time interval, but all tests must use the same criterion.

3. Plot dosage on the x-axis and performance (cc filtrate per minute) on the y-axis. The dosages and results can show 1 of 3 patterns:

    a. Performance increases with dosage, peaks, then gets worse with increasing dose. This is the desirable test result.
    b. Performance continues to increase with all dosages tested. This result indicates that the optimum dosage has not been reached. Additional tests should be conducted with higher dosages.
    c. Performance decreases with all increasing dosages. This result indicates that all dosages are beyond the optimum. Additional tests should be conducted with lower dosages. It may be necessary to use a more dilute polymer solution concentration.

4. After results are obtained below and above the optimum, plot all results and construct a curve through the points. The practical optimum is on the lower "shoulder" just before the optimum plateau is reached.

V. Mixing Sub Study Procedure

The purpose of Mixing Sub Study test is to examine the sensitivity of the floc formed by a particular polymer to shearing conditions. Conduct this test by following the steps below:

1. Select a 500 cc sample and place on laboratory multiple place mixer (Jar Test Machine)

2. Add the optimum polymer dose as determined previously and mix at 100 rpm for 3 minutes.

3. Run a Buchner funnel test and/or bench-scale filter test on the sample.

4. Compare these results to similar results from a low shear mixing test.

VI. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 10

Primary Sedimentation Column Testing (USACE ERDC/EL TR-03-1)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

ERDC/EL TR-03-1

Environmental Laboratory

US Army Corps of Engineers®
Engineer Research and Development Center

Evaluation of Dredged Material Proposed for Disposal at Island, Nearshore, or Upland Confined Disposal Facilities — Testing Manual

U.S. Army Corps of Engineers

January 2003

Approved for public release; distribution is unlimited.

B.4 Column Settling Tests for Effluent TSS/Turbidity

If turbidity or SS are identified as COCs, or if water quality standards (WQS) are specifically defined in terms of whole water (total) concentrations of COCs, settling tests are necessary to provide data for design or evaluation of disposal areas for retention of suspended solids and to compare to WQS (Figure B-2). These tests are designed to define the settling behavior of a particular sediment and to provide information concerning the volumes occupied by newly placed layers of dredged material. If WQS exist for turbidity, a sediment-specific correlation of suspended solids and turbidity must be developed (Thackston and Palermo 2000).

Sedimentation of freshwater slurries (mixtures of sediment and water) of concentration less than 100 g/L can generally be characterized as flocculent settling. As slurry concentrations are increased, the sedimentation process may be characterized as a zone settling process, in which a clearly defined interface is formed between the clarified supernatant water and the more concentrated settled material. Zone settling also occurs when the sediment/water salinity is approximately 3 parts per thousand (ppt) or greater. Flocculent settling also describes the behavior of residual suspended solids in the clarified supernatant water above the sediment/water interface for slurries exhibiting an interface. The procedures described below define the sedimentation of suspended solids under flocculent settling conditions or above the settled material/water interface under zone setting conditions. The settling test procedures consist of withdrawing samples from the settling column at various depths and times and measuring the concentrations of suspended solids. Additional data should be collected from the column settling test for purposes of CDF design for initial storage and minimum surface area for a given inflow rate. These procedures are provided in Engineer Manual 1110-2-5027 (USACE 1987).

B.4.1 Column settling test apparatus

An 8-in.-diam settling column such as shown in Figure B-3 is used. The test column depth should approximate the effective settling depth of the proposed disposal area. A practical limit on the depth of the test is 6 ft. The column should be at least 8 in. in diameter with interchangeable sections and with sample ports at 1/2-ft or closer intervals.

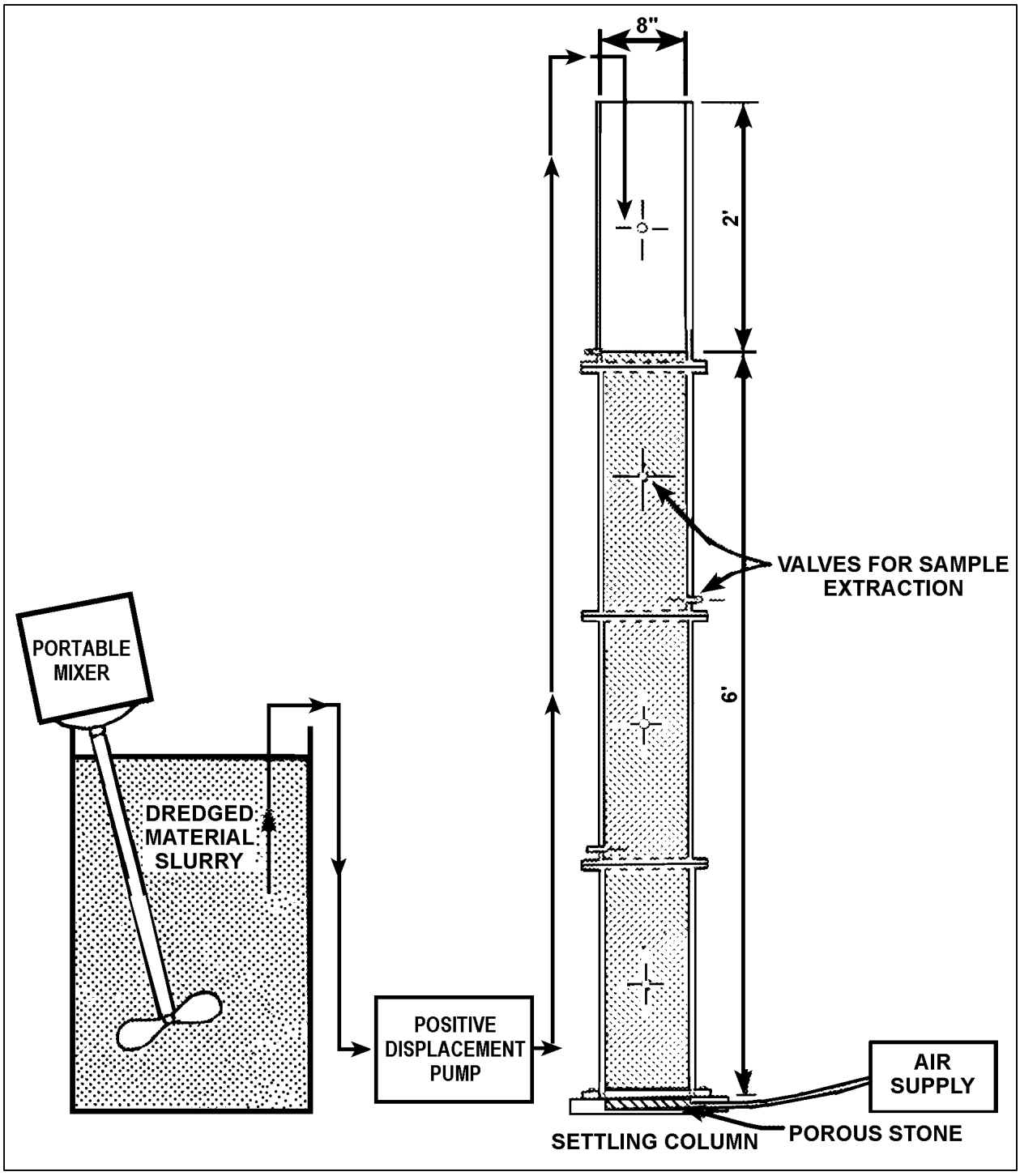


Figure B-2. Schematic of the Long Tube Column Settling Test

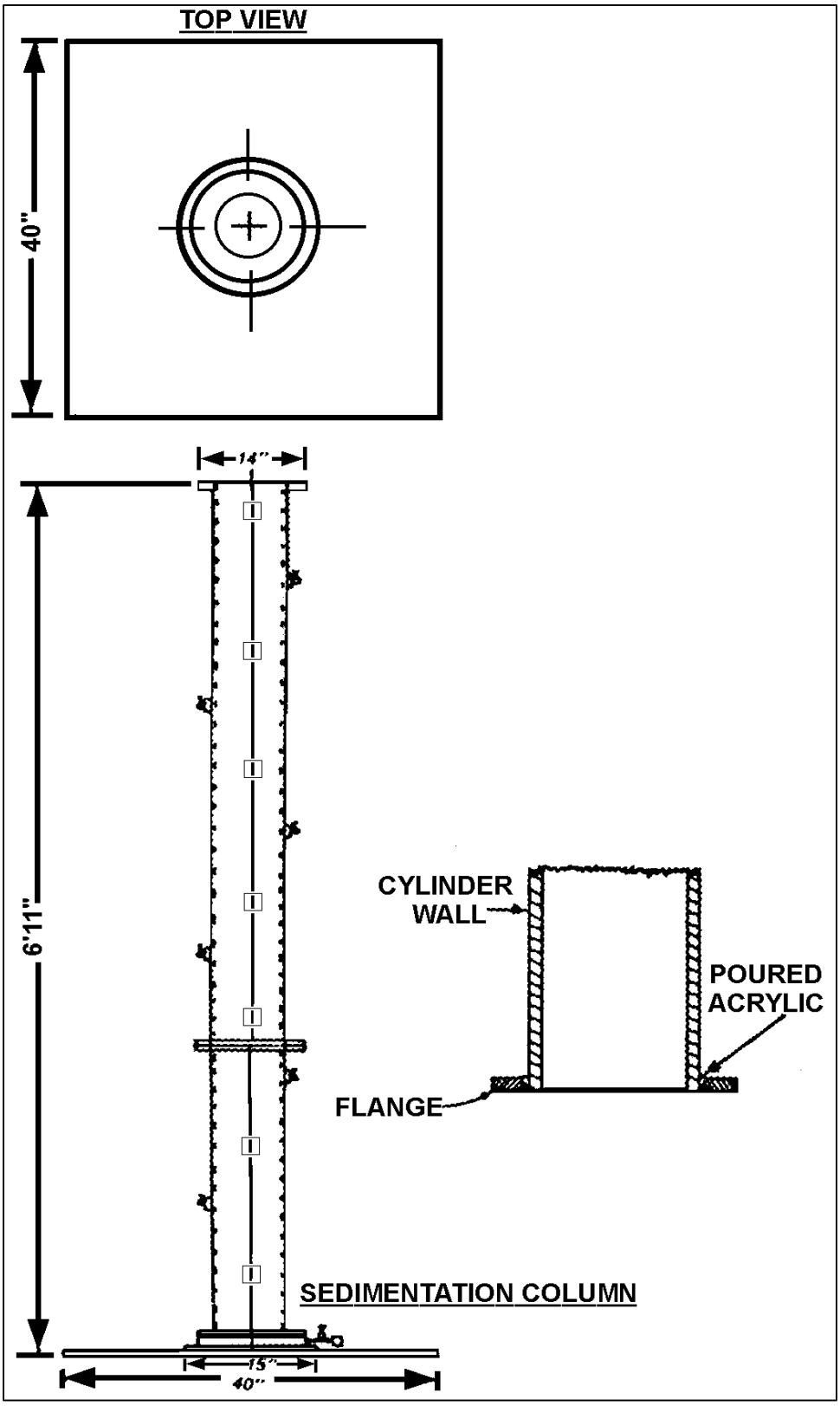


Figure B-3a. Specifications and plan for Long Tube Settling Column

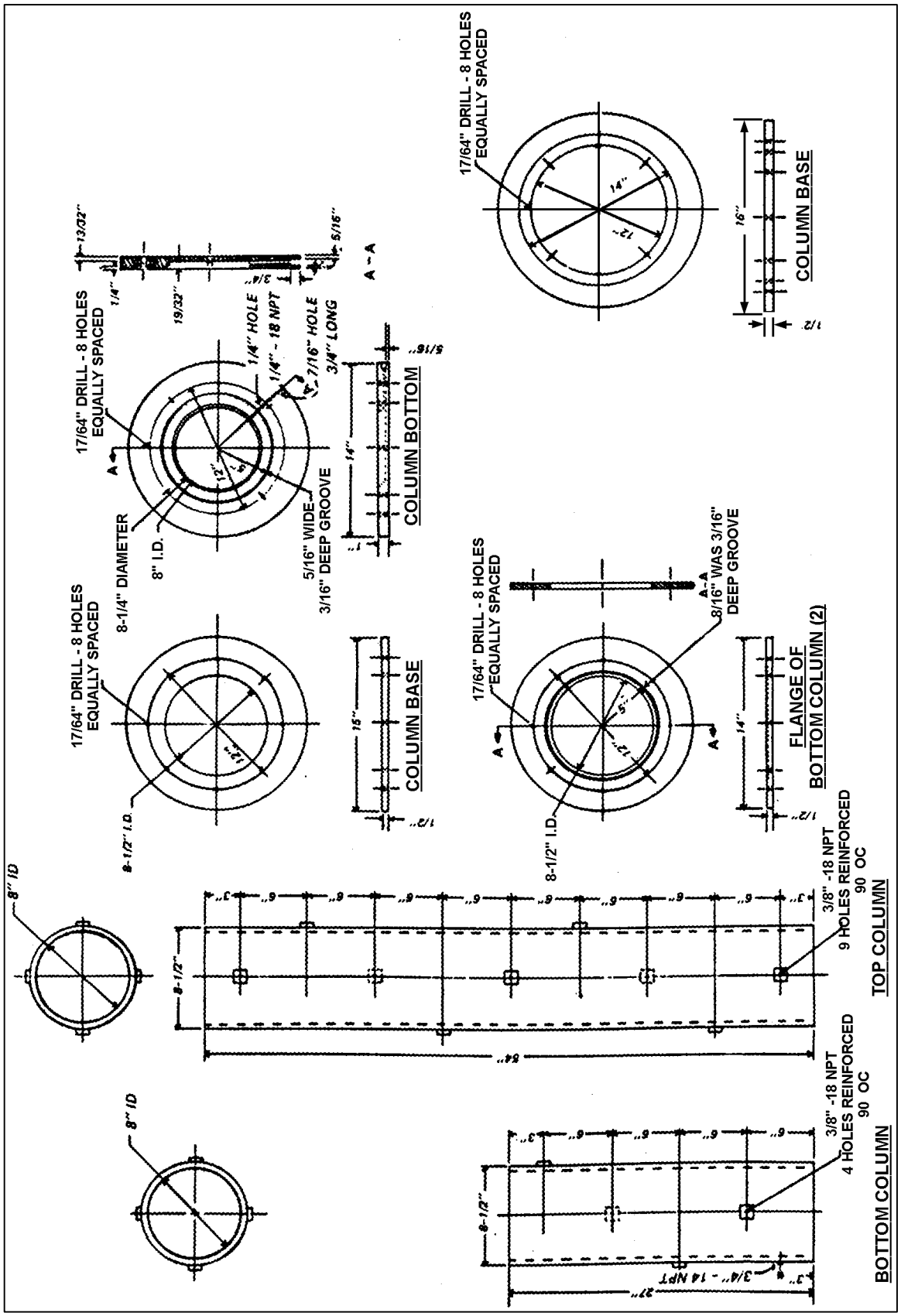


Figure B-3b. Plans for top and bottom sections of Long Tube Settling Column

B.4.2 Column settling test procedure

The following test procedure should be used:

Step 1. Mix the sediment slurry to a suspended solids concentration C equal to the expected concentration of the dredged material influent C_i. The slurry should be mixed in a container with sufficient volume to fill the test column. Field studies indicate that for maintenance dredging of fine-grained material, the disposal concentration will average about 150 g/L. This concentration should be used in the test if better data are not available.

Step 2. Pump or pour the slurry into the test column using compressed air or mechanical agitation to maintain a uniform concentration during the filling period.

Step 3. When the slurry is completely mixed in the column, stop the compressed air or mechanical agitation and immediately draw off samples at each sample port and determine their suspended solids concentration. Use the average of these values as the initial slurry concentration at the start of the test. The test is initiated with the drawing of the first samples.

Step 4a. If an interface has not formed during the first day, flocculent settling is occurring in the entire slurry mass. Allow the slurry to settle and withdraw samples from each sampling port at regular time intervals to determine the suspended solids concentrations. Record the water surface height and time at the start of the sampling period. Analyze each sample for total suspended solids. Substantial reductions of suspended solids will occur during the early part of the test, but reductions will decrease with longer retention times. Therefore, the intervals can be extended as the test progresses. Recommended sampling intervals are 1, 2, 4, 6, 12, 24, 48 hr, etc., until the end of the test. As a rule, a 50-m/L sample should be taken from each port. Continue the test until either an interface can be seen near the bottom of the column and the suspended solids concentration in the fluid above the interface is less than 1 g/L, or until the suspended solids concentrations in extracted samples shows no decrease.

Step 4b. If an interface forms the first day, zone settling is occurring in the slurry below the interface, and flocculent settling is occurring in the supernatant water. In this case, samples should be extracted from all side ports above the falling interface. The first of these samples should be extracted immediately after (a) the interface has fallen sufficiently below the uppermost port to allow extraction, or (b) a sufficient sample can be withdrawn from the surface without disturbing the interface. This sample can usually be extracted within a few hours after the beginning of the test. Record the time of extraction, water surface height, and port height for each port sample taken and analyze each sample for suspended solids. As the interface continues to fall, extract samples from all ports above the interface at regular time intervals. As before, a suggested sequence of sampling intervals would be 1, 2, 4, 6, 12, 24, 48, 96 hr, etc. The samples should continue to be taken until either the suspended solids concentration of the extracted samples shows no decrease or for a maximum time of 15 days. For this case, the suspended solids in the samples should be less than 1 g/L, and filtration will be required to determine the concentrations. The data should be expressed in milligrams per liter

for these samples. In reducing the data for this case, the concentration of the first port sample taken above the falling interface is considered the initial concentration.

B.5 References

Averett, D. E., Palermo, M. R., and Wade, R. (1988). "Verification of procedures for design of dredged material containment areas for solids retention," Technical Report D-88-2, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Brandon, D. L, Schroeder, P. R., and Lee, C. R. (1997). "Computerization of the decision-making framework effluent toxicity bioassay test results (LAT-E Program)," Technical Note EEDP-04-27, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Fulk, R., Gruber, D., and Wullschleger, R. (1975). "Laboratory study of the release of pesticide and PCB materials to the water column during dredging and disposal operations," Contract Report D-75-6, Envirex, Inc., under contract to the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Hayes, D. L., and Schroeder, P. R. (1992). "Documentation of the SETTLE module for ADDAMS: Design of confined disposal facilities for solids retention and initial storage," Technical Note EEDP-06-18, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Headquarters, U.S. Army Corps of Engineers (1987). "Confined disposal material," Engineer Manual 1110-2-5027, Washington, DC.

Kriezk, R. K., FitzPatrick, J. A., and Atmatzidis, D. K. (1976). "Investigation of effluent filtering systems for dredged material containment facilities," Technical Report D-76-8, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Montgomery, R. L., Thackston, E. L., and Parker, F. L. (1983). "Dredged material sedimentation basin design," *Journal of Environmental Engineering, American Society of Civil Engineers* 109(2).

Palermo, M. R. (1985a-d). "Interim guidance for predicting quality of effluent discharged from confined dredged material disposal areas," EEDP-04-01 through 04-4, U.S. Army Engineer Waterways Experiment Station, Environmental Laboratory, Vicksburg, MS.

Palermo, M. R., and Schroeder, P. R. (1991). "Documentation of the EFQUAL module for ADDAMS: Comparison of predicted effluent quality with standards," Technical Note EEDP-06-13, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Palermo, M. R., and Thackston, E. L. (1988a). "Test for dredged material effluent quality," *Journal of Environmental Engineering, American Society of Civil Engineers* 114(6).

_____. (1988b). "Verification of predictions of dredged material effluent quality," *Journal of Environmental Engineering, American Society of Civil Engineers* 114(6).

_____. (1988c). "Flocculent settling above the zone settling interface," *Journal of Environmental Engineering, American Society of Civil Engineers* 114(4).

Schroeder, P. R., and Palermo, M. R. 2000. "The automated dredging and disposal alternatives management system (ADDAMS)," Environmental Effects of Dredging Technical Note EEDP-06-12 (Revision of 1990), U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Schroeder, P. R., Palermo, M. R., and Olin-Estes, T. J. "Screening evaluations for confined disposal facility effluent quality," Environmental Effects of Dredging Technical Note EEDP (in preparation), U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Thackston, E. L., and Palermo, M. R. (2000). "Improved ,ethods for correlating turbidity and suspended solids for monitoring," DOER Technical Notes Collection, ERDC TN-DOER-E8, U.S. Army Engineer Research and Development Center, Vicksburg, MS. *www.wes.army.mil/el/dots/doer*

U.S. Army Corps of Engineers/U.S. Environmental Protection Agency. (1992). "Evaluating environmental effects of dredged material management alternatives - A technical framework," EPA842-B-92-008, Washington, DC.

U.S. Environmental Protection Agency/U.S. Army Corps of Engineers. (1995). "QA/QC guidance for sampling and analysis of sediments, water, and tissues for dredged material evaluations - chemical evaluations," EPA-823-B-95-001, Washington, DC.

U.S. Environmental Protection Agency/U.S. Army Corps of Engineers (1998). "Evaluation of dredged material proposed for discharge in waters of the U.S. – testing manual," EPA-823-B-98-004 Office of Water (4305), Washington, DC.

Appendix 11

SOP – Buchner Funnel Tests (Standard Method 2710H)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

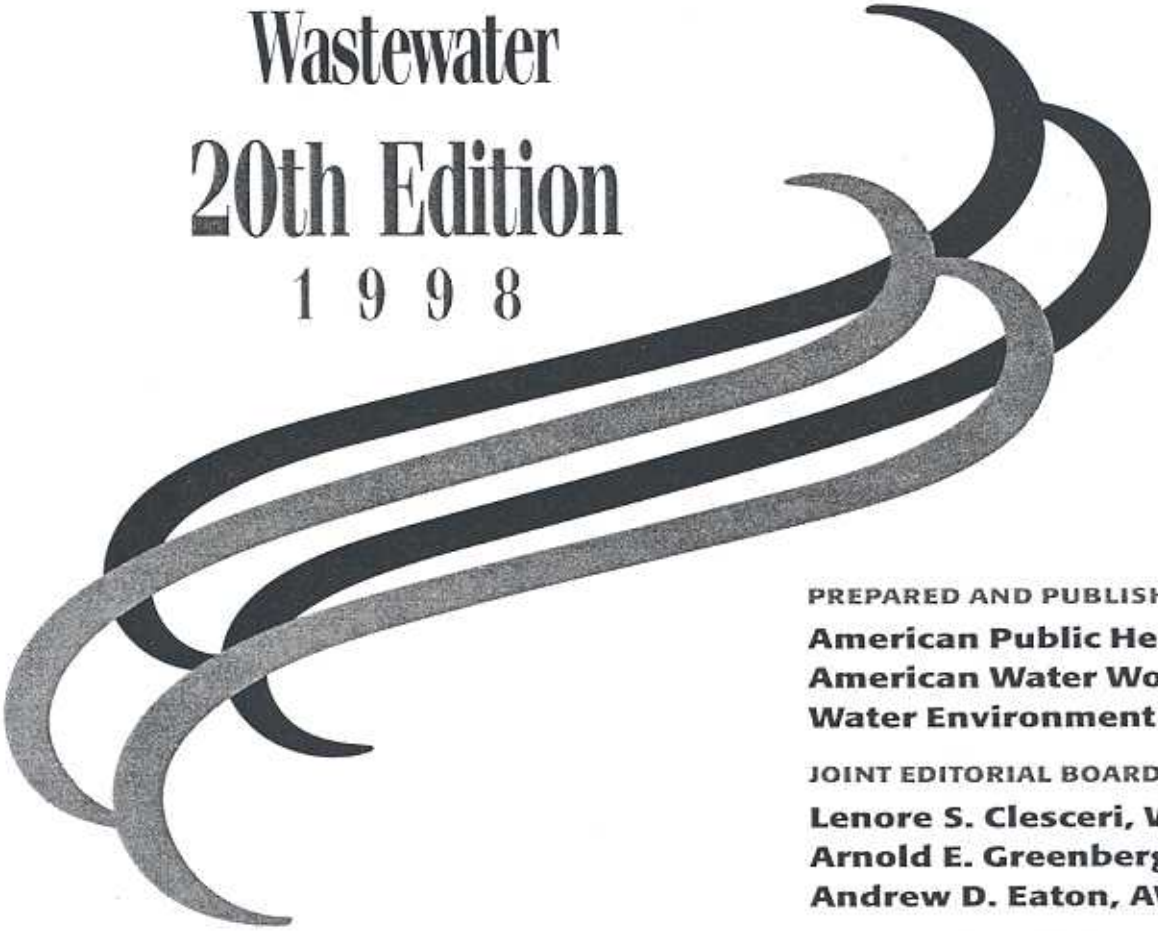
Standard Methods

FOR THE

Examination of Water and Wastewater

20th Edition

1998



PREPARED AND PUBLISHED JOINTLY BY

American Public Health Association
American Water Works Association
Water Environment Federation

JOINT EDITORIAL BOARD

Lenore S. Clesceri, WEF, Chair
Arnold E. Greenberg, APHA
Andrew D. Eaton, AWWA

MANAGING EDITOR

Mary Ann H. Franson

PUBLICATION OFFICE

American Public Health Association
1015 Fifteenth Street, NW
Washington, DC 20005-2605

toring operation of a dewatering process, avoid this effect by ensuring homogeneity among sludge samples. Comparison of CST data from different sludge samples from the same source (especially if taken on different days) cannot be made with confidence unless suspended solids concentrations are comparable. Make a rough correction for different solids contents by dividing the sludge's CST value by its corresponding solids concentration.

Characteristics of CST paper may vary between lots. If comparison of CST values for distilled water indicates such variations, subtract times for distilled water blanks from sample times to improve comparisons.

Record CST model used, paper type, sludge type, sludge temperature, and capillary suction time. Measure solids concentration and CST of distilled water using the same paper to provide useful information.

4. Precision and Bias

Ten tests conducted on an anaerobically digested pulp mill sludge resulted in a mean CST of 363.2 s with a standard deviation of 36.2 s. Twenty tests using an anaerobically digested municipal wastewater sludge gave a mean of 85.2 s with a standard deviation of 14.12 s. Triplicate analyses of 30 sample sets of conditioned and unconditioned alum sludge resulted in an average standard deviation of 1.0 s with means between 5 and 80 s. Method bias cannot be determined.

5. Bibliography

BASKERVILLE, R.C. & R.S. GALE. 1968. A simple automatic instrument for determining the filtrability of sewage sludges. *J. Inst. Water Pollut. Control* 67:233.

KAVANAGH, B.A. 1980. The dewatering of activated sludge: measurements of specific resistance to filtration and capillary suction time. *Water Pollut. Control* 79:388.

VESILIND, P.A. 1988. Capillary suction time as a fundamental measure of sludge dewaterability. *J. Water Pollut. Control Fed.* 60:215.

TILLER, F.M., Y.L. SHEN & A. ADIN. 1990. Capillary suction theory for rectangular cells. *Res. J. Water Pollut. Control Fed.* 62:130.

2710 H. Time-to-Filter

1. General Discussion

The time to filter (TTF) correlates with capillary suction time (CST) and is similar to the specific resistance to filtration if sludge solids content and filtrate viscosity do not vary among compared samples. The test requires approximately 200 mL sludge and can be used to assist in the daily operation of sludge dewatering processes or to evaluate sludge-conditioning polymers and dosages.

Testing with a smaller volume is possible in applications to evaluate water drainage rate subsequent to jar tests and settleable solids determination (see Section 2540F). In this case, drain collected sludge from one or more Imhoff cones after decanting as much supernatant as possible; use a small-volume TTF apparatus.

The test consists of placing a sludge sample in a Buchner funnel with a paper support filter, applying vacuum, and measuring the time required for 100 mL filtrate (or, for reduced sample volumes, 50% of original sample) to collect. While similar to the specific resistance to filtration test, the time-to-filter test is superior because of its ease of use and simplicity.

2. Apparatus

a. Time-to-filter large-volume or small-volume (Figure 2710:4) *assembly.*

*b. Filter paper**

c. Stopwatch.

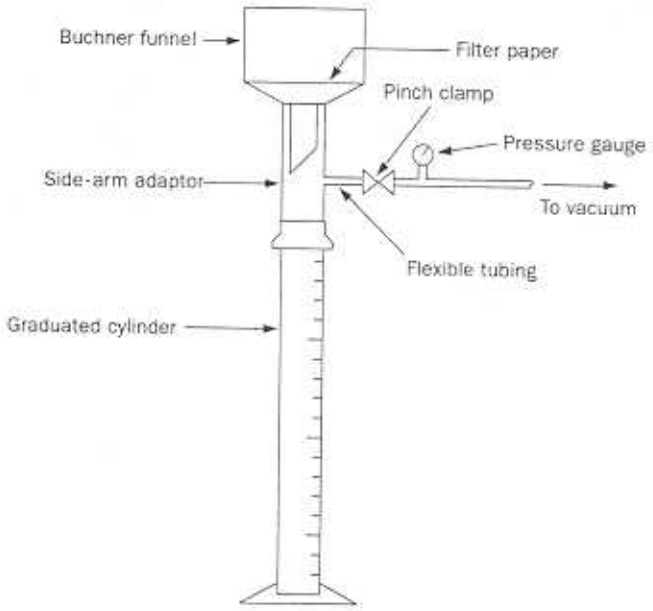


Figure 2710:4. TTF equipment. Large-volume equipment requires a 9-cm-diam Buchner funnel and a 250-mL graduated cylinder. Small-volume equipment requires a 2.5-cm-diam funnel and a 10-mL cylinder.

3. Procedure

Place paper filter in funnel and make a firm seal by pre-wetting with a small volume of water with vacuum on. If using large-volume apparatus, take a 200-mL sample of sludge. With vacuum pump providing a constant vacuum of 51 kPa, pour sample into funnel. Start stopwatch or timer and determine time required for 100 mL of sample to collect in graduated cylinder. This is the time to filter. Make a minimum of three replicate determinations.

For the small-volume test, use 7 to 10 mL sludge. Record time required for 50% of sample to collect in graduated cylinder. Compare this time to filter only to other results using the same sample volume.

* Whatman No. 1 or 2 or equivalent.

Sludge suspended solids concentration has a significant effect on test results. In evaluating sludge-conditioning products, compare results for which initial suspended solids concentrations are comparable. Make a rough correction for different solids contents by dividing the time-to-filter value by its corresponding solids concentration. However, variations in solids concentration occur in full-scale applications, and the time-to-filter results may be interpreted as indicating the overall rate of water release from sludges, including the effect of differing solids concentrations.

4. Precision and Bias

Variations in vacuum pressure, support filter type, sludge temperature, and sample volume can affect test results. Triplicate analyses of 18 sample sets of conditioned and unconditioned alum sludge resulted in an average method precision of 19 s (approximately 4% of the average value) for the large-volume TTF test. Triplicate analyses of 9 sample sets of conditioned and unconditioned alum sludge resulted in a method precision of 9 s (approximately 6% of the average value) for the small-volume TTF test. Method bias, which refers to the agreement between the value determined by the test method and the real value, cannot be determined.

5. Bibliography

KNOCKE, W.R. & D.L. WAKELAND. 1983. Fundamental characteristics of water treatment plant sludges. *J. Amer. Water Works Assoc.* 113: 516.

DENTEL, S.K., T.A. BOBER, P.V. SHETTY & J.R. RESTA. 1986. Procedures Manual for Selection of Coagulant, Filtration, and Sludge Conditioning Aids in Water Treatment. Publ. 90515, American Water Works Assoc., Denver, Colo.

2720 ANAEROBIC SLUDGE DIGESTER GAS ANALYSIS*

2720 A. Introduction

Gas produced during the anaerobic decomposition of wastes contains methane (CH_4) and carbon dioxide (CO_2) as the major components with minor quantities of hydrogen (H_2), hydrogen sulfide (H_2S), nitrogen (N_2), and oxygen (O_2). It is saturated with water vapor. Common practice is to analyze the gases produced to estimate their fuel value and to check on the treatment process. The relative proportions of CO_2, CH_4, and N_2 are normally of most concern and the easiest to determine because of the relatively high percentages of these gases.

1. Selection of Method

Two procedures are described for gas analysis, the volumetric method (B), and the gas chromatographic method (C). The volumetric analysis is suitable for the determination of CO_2, H_2, CH_2, and O_2. Nitrogen is estimated indirectly by difference. Although the method is time-consuming, the equipment is relatively simple. Because no calibration is needed before use, the procedure is particularly appropriate when analyses are conducted infrequently.

The principal advantage of gas chromatography is speed. Commercial equipment is designed specifically for isothermal or temperature-programmed gas analysis and permits the routine separation and measurement of CO_2, N_2, O_2, and CH_4 in less than 15 to 20 min. The requirements for a recorder, pressure-regulated bottles of carrier gas, and certified standard gas mixtures for calibration raise costs to the point where infrequent analyses by this method may be uneconomical. The advantages of this system are freedom from the cumulative errors found in sequential volumetric measurements, adaptability to other gas component analyses, adaptability to intermittent on-line sampling and analysis, and the use of samples of 1 mL or less.[1]

2. Sample Collection

When the source of gas is some distance from the apparatus used for analysis, collect samples in sealed containers and bring to the instrument. Displacement collectors are the most suitable containers. Glass sampling bulbs (or tubes) with three-way glass or TFE stopcocks at each end, as indicated in Figure 2720:1, are particularly useful. These also are available with centrally located

* Approved by Standard Methods Committee, 1997.

Appendix 12

SOP – Bench-scale Pressure Filter Tests

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Bench-scale Pressure Filter Tests

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for the bench-scale pressure filter tests. These tests are part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

Bench-scale pressure filter tests are used to simulate the performance of full scale facilities. They are especially useful for evaluating chemical treatment programs or comparing the performance of different chemical treatment products.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- 75 mm x 75 mm plate filter press (U.S. Filter, or similar- see attached diagram for example apparatus);
- Compressed air source; and
- Beakers.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Procedure for the 75 mm Filter Press Tests

Select filter media cloth and place it on both sides of the filter press chamber. Close the chamber with the hydraulic closure hand pump. Attach the feed connection from the pressure reservoir to the feed inlet of the filter housing.

Apply polymer dose to 0.5 L of sediment sample and mix by pouring between beakers until full floc formation is observed. Add the flocculated sample to the pressure reservoir of the bench scale filter press.

Apply compressed air to the pressure reservoir and begin timer. Measure filtrate volume at 1-minute intervals until filtration rate drops below 5 mL per min. Release pressure and open filter housing. Remove filter cake.

Submit cake and filtrate samples for analyses indicated in the TS Work Plan.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 13

SOP – Cake Release Screening – Filter Leaf Tests (Perlmutter, 2003)

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

(04/03) Test it Right

The appropriate testing procedures can help direct the selection of pressure or vacuum filtration equipment and ensure optimum equipment operation

Barry A. Perlmutter
April 11, 2003

Solid–liquid separation by pressure or vacuum, cake washing and drying are integral to producing a chemical or pharmaceutical product or for fluid clarification and recovery. A number of competing technologies and options can be employed to accomplish these steps, including nutsche filters, centrifuges, belt filters, filter presses, pressure plate filters and others. This article concentrates on the testing of pressure or vacuum operations. Centrifugation testing is conducted in a similar manner, generally using a bucket "bench-top" centrifuge to gather data.

In solid–liquid separation systems, a wide variety of parameters influence performance. Evaluation and testing procedures can help plants determine the effectiveness of a particular system. Parameters that can be evaluated include particle size and shape, particle type, density, concentration, viscosity, cake height, pressure or vacuum, filter media, batch or continuous operation, required production throughput and more.

Theoretical calculations of filtration performance (Darcy's Equation and other modeling techniques) are far from easy, but can be useful. Creative problem-solving, however, continues to be a primary task of process engineers. The selected internal or external filtration testing personnel must have the ability to combine theory and practice.

Pocket-leaf filter testing
Bench-top testing first must be used to narrow the gap between theory and practice and to begin the equipment selection process. A useful bench-top filter system is a pressurized pocket-leaf filter (PLF), which resembles a Buchner funnel. The figure shown on the next page illustrates a typical PLF unit.

The PLF shown has a filter area of 0.002 square meters (sq m) and consists of a pressure vessel (90 pounds per square inch [psig] to full vacuum), a top cover with a pressure gauge and gas (or air) connection and a bottom base for the filter media and filtrate outlet. The pressure vessel and base are jacketed and can be heated or cooled with a heat-transfer medium. The filter media can be synthetic single-layer metal or multi-layer sintered metal. The materials of construction are 316 Ti stainless steel, Hastelloy or polypropylene, and the fill volumes range from 250 milliliters (ml) to 2,000 ml.

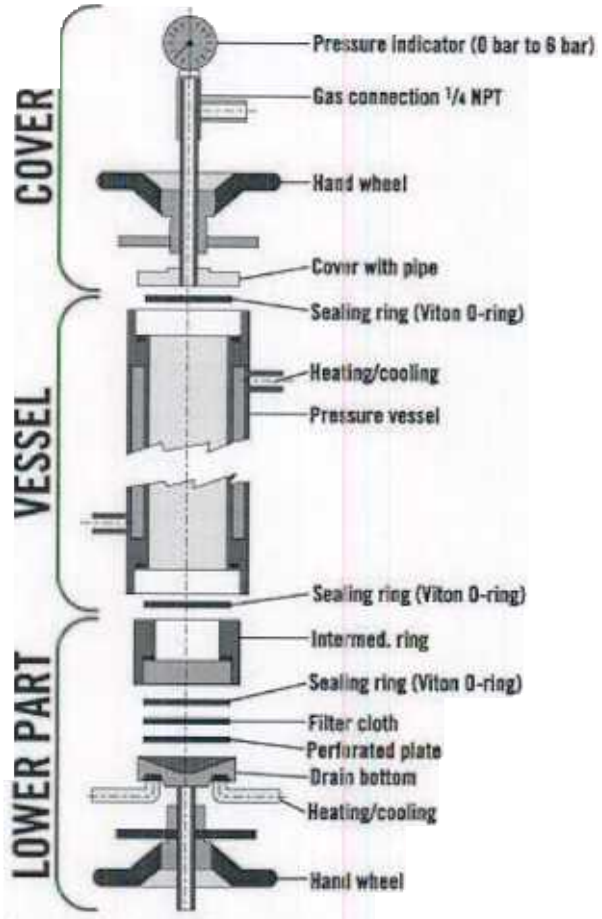
A number of items are required for accurate PLF testing, including:
- Material Safety Data Sheets (MSDSs) for all materials.
- 4,000 ml to 8,000 ml of representative-quality feed material for each material to be tested.
- 2,000 ml of wash material for each wash.
- A 1,000 ml to 4,000 ml closed container with mixer to use for the feed material before each run.
- Several 250 ml to 500 ml containers for the feed material, the filtrate, the fresh wash material and the wash filtrates.
- Small containers for the filter cake.
- A gram scale.
- A vacuum oven or other technique to check the percent solids in the feed slurry, filtrate (mother liquor) and wash filtrates, as well as the percent moisture in the filter cake by a Karl-Fischer analysis or other technique.
- Gloves and breathing equipment.
- A regulated air or gas supply that can be controlled at 90 psig.
- A flowmeter on the air or gas supply. The flowmeter allows the air or gas flow rate to be measured during the drying step.
- A heat-transfer medium (hot oil, glycol, steam or cooling liquid).
- A vacuum source.
- A specific test apparatus to measure data such as pH, conductivity, particle size after completion of the testing cycle, etc.

Representative Sample. The sample must be representative of what is to be found in the actual process, including particle size distribution, particle shape, viscosity, temperature, etc.

Testing location and personnel. Several options are available for the testing location. The first option is the plant's lab or pilot plant. This approach offers the best chance of a representative sample and provides easy access for all process engineers involved in the project. However, testing often will conflict with the plant's production requirements. Furthermore, time conflicts could exist, so it is important to determine who would conduct the testing at the plant site — the plant's or the vendor's process engineers. If it is the vendor's engineer, then safety training, laboratory access and other concerns must be addressed.

A second alternative is to conduct the tests at the vendor's laboratory using process materials produced at the plant. This approach allows focused testing with little or no interruptions. In this case, it is important for the process engineer(s) to evaluate the vendor's laboratory, as well as the vendor's process personnel who will be conducting the tests. If possible, the plant's process engineer(s) should be invited to witness and help perform the tests; they will be familiar with the "quirks" of the process and product.

PLF Unit



Source: BHS-Filtration Inc.

A third alternative combines the first two approaches. Both the process reaction and the filtration tests are performed in the vendor's laboratory. In this case, either the vendor or the plant process engineer(s) would supply the necessary process chemicals to conduct the reactions and/or precipitations. The resulting slurry then would be fed immediately to the PLF to begin the testing.

This approach offers benefits in that the sample is representative, the testing is focused, reaction/precipitation parameters can be modified to improve the filtration results, and a holistic approach to testing is implemented.

Table 1: Typical Data Collection Form for PLF Tests

Customer:_____ Test Number:_____

Date:_____ Test Unit:_____

		UNITS	Run#	Run#	Run#	Run#	Run#
	Filter media :						
	Suspension:						
Filling	Volume of slurry						
	Density of slurry						
	% Solids in feed						
Filtration	Pressure						
	Temperature						
	Volume of filtrate						
	Time for filtration						
	% Solids in filtrate						
Wash 1	Wash material						
	Pressure						
	Temperature						
	Volume of filtrate						
	Time for filtration						
	% Solids in filtrate						
Wash 2	Wash material						
	Pressure						
	Temperature						
	Volume of filtrate						
	Time for filtration						
	% Solids in filtrate						
Wash 3	Wash material						
	Pressure						
	Temperature						
	Volume of filtrate						
	Time for filtration						
	% Solids in filtrate						
Drying	Pressure						
	Temperature						
	Flow rate						
	Time for drying						
Cake	Weight						
	Thickness						
	% Residual moisture						
	Discharge OK?						
	Cake rests on filter cloth?						

Source: BHS-Filtration Inc.

Required data and data collection. The testing objectives could be to expand plant production, decrease cycle times, maximize wash efficiencies or achieve another goal. Table 1 shows a typical data collection form that can be used for bench-top testing with the PLF unit. Table 2 illustrates the data about the process that are required, slurry, washing media and, most importantly, the testing objectives.

Testing procedures

Pressure or vacuum filtration. The first optimization is the filtration rate. A premeasured amount of slurry is added from the top. Pressure or vacuum filtration begins, and the amount of filtrate vs. time is recorded.

Parameters that are varied sequentially in this step include cake depth, filtration pressure or vacuum and filter media. For thin-cake filtration technologies, cake depths can vary between 5 millimeters (mm) and 25 mm. Maximum cake thickness for the PLF unit is 150 mm.

Displacement washing. Displacement washing is performed after the filtration step is completed. A measured amount of wash liquid is added carefully in a predetermined wash ratio so the cake is not disturbed. Once again, pressure and time are measured. One or more wash tests can be conducted with the same or different wash liquids.

Cake pressing. Several thin-cake technologies can perform cake pressing or squeezing. The PLF can simulate this pressing procedure with a "pressing plug." The pressing plug is actuated by nitrogen pressure and squeezes the cake onto filter media. This pressing can be conducted before, during or after the filtration, washing and drying steps.

Drying. Product drying in the PLF is tested by blowing ambient-temperature or hot gas through the cake or via vacuum. In addition, both the vessel jacket and base jacket are heated to simulate a production unit. The pressure is kept constant, and gas throughput is measured vs. time. After a preselected drying time, the cake is removed, and the cake depth and weight are determined. The cake then is analyzed for moisture content. Several iterations are required.

Results and analysis. Once testing is completed, the vendor's process engineers analyze the data to recommend one or more filtration technologies. The test report includes an executive summary, test objectives, test methods and facilities, test data (in table form), test results (in written and graphical form, including filtration and drying curves), recommendation of production equipment and scale-up and any other recommendations and "path-forward" action steps.

Based on the PLF tests and recommendations, pilot-scale tests can be conducted. These tests should most often be conducted at the plant site using actual feed material from the reactor, as well as the actual washing and drying media, operating conditions, etc.

It is also important for the plant to ensure the same vendor engineer who conducted the PLF tests conducts the pilot tests. The testing procedure and testing "tricks" employed on the bench-top, therefore, also will be employed in the pilot testing.

Table 2: Application Process Data Information

Material: (name of the suspension)_____

I. Filter operation
1. The product is the: ❑ liquid ❑ solid ❑ both
2. What is the current method of filtration?_____
3. What needs to be improved ?_____

II. Production rates
___Continuous
1. Suspension_____ m^3/hr
2. Dry solids_____ kg/hr
3. Washing agent_____ m^3/hr
4. Daily production time_____ hr/day

OR

___Batch
1. Suspension/batch_____ m^3
2. Dry solids/batch_____ kg
3. Washing agent/batch_____ m^3
4. No. batches/day_____
5. Allowable batch time_____ hr

III. Suspension
1. Density_____ g/l
2. Solids content_____ g/l
3. Average particle size_____ microns
4. Temperature_____ deg. C
5. Viscosity_____ m^2/sec
6. pH_____
Composition a) liquid:_____
b) solids:_____
Type of solids: ❑ crystalline ❑ amorphous ❑ fibrous ❑ colloidal

IV. Filter cake
1. Desired residual moisture in the filter cake_____ %
2. Desired degree of washing_____
3. Permissible temperature for moisture determination_____ deg. C
4. What happens to the filter cake when it is discharged?_____

V. Filtrate
1. Allowable solids content_____ g/l
2. What happens to the filtrate when it is discharged?_____

VI. Washing
1. What wash agent will be used ?_____ at ____ deg. C
2. Allowable quantity_____ m^3/hr or _____ l/kg of dry solids
3. Required specification of the filtrate produced _____
4. Will counter-current washing be required ? ❑ no ❑ yes, with____ stages
5. What happens to the wash filtrate when it is discharged?_____

VII. Recommended materials of construction
1. Metals:_____
2. Synthetic materials, elastomers:_____
3. Seals:_____
4. Filter cloth:_____

VIII. Comments_____

Source: BHS-Filtration Inc.

Conclusions

Currently, the most efficient approach to selecting and/or optimizing a pressure or vacuum filtration system is to use a PLF unit. With assistance and process support from the vendor and accurate data from the testing — combined with filtration theory and experience — proper selection, scale-up, optimization and process guarantees can be realized.

Perlmutter is president and managing director of BHS-Filtration Inc., Charlotte, N.C. Contact him at barry.perlmutter@ bhs-filtration.com.

© 2003 Putman Media

Appendix 14

SOP – Plate and Frame Filter Test

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Plate and Frame Filter Tests

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for the plate and frame (P&F) filter tests. These tests are part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

The main purpose of the plate and frame filter tests is to develop sizing data for full-scale facilities. The pilot study is also intended to demonstrate performance characteristics such as filtrate quality and cake dryness. Polymer performance is expected to have a major impact on system operations. Successful operating of a dewatering system is often a direct result of the operator's skill in reacting to changes in solids loadings and responding with corresponding modifications to polymer dosages.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- 250 mm pilot plate and frame filter press (U.S. Filter, or similar) with 100 psig pump; and
- Feed tank, 100 L,, or 55-gal drum, with variable-speed mixer.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Procedure for the 250 mm Plate & Frame Filter Tests

1. P&F Filter Test

Select polymer and optimum dosage (mg polymer per Kg solids) from bench-scale filter press tests. Apply polymer dosage to the feed tank, with mixing at velocity gradient, G, of 50 to 200 sec^{-1}. After floc is formed, slow the mixer to G of 50 /sec or minimum sufficient to maintain a uniform slurry concentration.

Select filter cloth media based on previous results of the filter leaf testing and/or bench-scale filter press. Different filter cloths can also be tested on the filter press.

Follow the supplier's operational summary (US Filter, attached), to start the feed, monitor pressure and filtration rate, stop the feed, open the press, and discharge cake.

Submit cake and filtrate samples for analyses indicated in the TS Work Plan.

2. Cake Solids vs. Time Sub-Study Tests

In this series of tests, the filtration run is intentionally terminated early to observe the cake solids and acceptability for landfilling. If slightly wetter cake is still acceptable for landfilling, there may be opportunities for smaller or fewer presses. Repeat pressure filtration runs for samples indicated in the TS Work Plan using the procedures described above.

3. High Volume P&F Runs for Column/MMF Feed

The main purpose of this series of runs is to produce sufficient volumes of filtrate for subsequent testing of multimedia filter columns and pilot carbon adsorbers. Total feed slurry from 200 to 500 L (53 to 130 gal) will be required. The 55-gal feed tank will need to be recharged and treated with polymer for each recharge. Repeat pressure filtration runs for samples indicated in the TS Work Plan using the procedures described above.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

USFilter
Dewatering Systems

2155 112TH AVENUE TEL 616 772-9011
HOLLAND, MI 49424 FAX 616 772-4516

250mm PILOT FILTER PRESS OPERATIONAL SUMMARY

1. Close press making sure no cloths are folded over.
2. Clamp press to 6,000 psig.
3. Start slurry feed pump at 25 psig.
4. As the pump slows down, increase the slurry feed pump pressure 25 psig . Continue to do this until the maximum pressure is achieved (not to exceed 100 psig).
5. Stop the pump when there is 20-45 seconds between strokes or when the terminal flow rate is reached.
6. Close the valve on the center feed.
7. Perform a 40 psig air blowdown of the filter cake from the top left connection on the manifold for ten minutes. All valves are closed except for the bottom right valve. Measure the total volume of liquid discharged during the air blowdown.
8. Open the press and drop the cakes into the cake pan.
9. Weigh the cake.

Test Slurry for: Total suspended solids (mg/l)
Test Cake for: Total Solids (% by wt.)

Record, at a minimum, the following information during the test on the Press Field Record Sheet:

Slurry Solids Concentration (mg/l)
Slurry Temperature
Filtrate out vs Time and Pressure
Total Air Blowdown Time
Total Air Blowdown Water Out
Weight of Filter Cake
Cake Thickness
Solids Concentration of the Filter Cake.

Appendix 15

SOP – Laboratory Centrifuge Tests

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Laboratory Centrifuge Tests

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for the laboratory centrifuge tests. These tests are part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan, December 2003).

Centrifuges are not commonly used to dewater dredged sediments. However, they may be cost-effective for some sediment environments and they are retained as an alternative dewatering process. Centrifuge screening tests will be conducted on hydraulically dredged or mechanically dredged, but hydraulically unloaded dredged material slurry simulations.

Filter press feed simulations (H1S4, H2S3, and H2S4), presented on Table 2 of the TS Work Plan, and 2 polymer treatment conditions will be screened using a laboratory centrifuge capable of handling at least 0.5-liter volumes. A laboratory centrifuge is not sufficient to develop full-scale performance or design conditions; however, centrate residual suspended solids and cake moisture content can be compared to filter press or belt press results.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003); and
- Laboratory centrifuge capable of handling 0.5-liter test volumes.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Procedure for Laboratory Centrifuge Tests

Review the results of polymer screening and optimization tests for belt press and plate & frame filter press applications. Based on those results, and in consultation with centrifuge and polymer vendors, select four polymer doses (mg polymer per Kg of solids) to test in the laboratory centrifuge screening tests. Include a control sample with no polymer added.

Apply measured polymer doses to 500-ml samples of simulated dredge slurry in 1-liter beakers on a multiple place stirrer with 1 in. x 3 in. paddle. Polymer samples should all be diluted to the same volume (25 mL) with water before dosing the sediment; this same volume should be added to the control sample. Stir at rotational speed of 40 to 60 rpm, corresponding to the velocity gradient, G, of 50 to 100 /sec. Maintain mixing for 5 minutes or modify mixing conditions based on observations of floc formation and/or shear. Note final mixing conditions used in testing.

Following flocculation, place samples in centrifuge tubes and place in the laboratory centrifuge. Follow centrifuge manufacturer's instructions and step up to 3,500 rpm. Hold this speed for 15 minutes, then follow the manufacturer's shutdown procedures.

Decant centrate and measure decanted centrate volume. Submit centrate for analysis of:

- PCB (GEHR Modified Method 8082); and
- TSS (USEPA 160.2).

Remove centrifuge cakes. Based on centrate clarity, select cake corresponding to optimum dosage and submit this cake sample for analysis of:

- PCB (GEHR Modified Method 8082); and
- Water content (USEPA 160.3).

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 16

SOP – Mixing Energy Study

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Mixing Energy Study

I. Scope and Application

This standard operating procedure (SOP) describes the procedures for conducting Mixing Energy Studies for use in treatability studies, as described in the Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

During processing of Hudson River dredged material, it may be necessary to store dredged slurries for various reasons. Storage may be necessary to equalize dredged volumes that are dredged and treated at different rates and durations. Storage may also be necessary to allow dredging to proceed during processing facility downtimes. Upon storage, dense sediment particles will settle and compact, making it difficult to move them to subsequent treatment processes. Either the particulates must be slurried for removal or they must be removed as a denser sediment.

Equalization/holding facilities and mixer design will be based on anticipated dredged material properties, such as solids concentrations, specific gravity, and particle size distribution. The Mixing Energy Study is intended to provide verification of equipment supplier recommendations or calibration points for design calculations.

Mixing energy is usually defined by the velocity gradient, G, expressed as sec^{-1}, as originally proposed by Camp and Stein in 1943. Velocity gradient can be calculated from measuring or estimating mixer horsepower imparted. Velocity gradient can also be estimated from curves prepared for specific tank or container configurations, baffles, and impeller shapes.

Specific dredged slurry simulations to be used in the mixing energy study are presented in Table 2 of the TS Work Plan.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (BBL, 2003);
- Multiple-place stirrer and 2-L containers (beakers or square dimensions, with or without baffles);
- 55-gallon drums and variable-speed mixers and motors;
- 25-mL pipettes and vacuum bulbs; and
- Laboratory notebook.

III. Health and Safety Considerations

Refer to the Revised HASP (BBL, 2003).

IV. Mixing Energy Study Procedure

In this test, slurry samples are subjected to mixing conditions that can be quantified by calculating velocity gradient, G, expressed as sec^{-1}. For each test, samples from near the surface are withdrawn and analyzed for suspended solids content. This measurement is compared to suspended solids content in a thoroughly mixed sample.

The procedures for conducting a Mixing Energy Study are described below:

1. Select five dredge slurry simulations for Mixing Energy Study, as shown on line for DQO 4b. (5) and DQO 4c. (5) of Table 2 in the TS Work Plan.

2. Thoroughly mix dredge slurry simulations and place 2 L of each in a 2L beaker. Also take a 25-mL sample of each mixed dredge slurry simulation to measure initial suspended solids concentration.

3. Place containers on multiple-place stirrer with blades configured as shown in Figure 3 (Lai et al., 1975).

4. Stir at speeds corresponding to mixing intensity, G, of 200, 500, and 1,000 sec^{-1}. At each speed, acquire a sample from beneath the surface at a depth of 20% of the full water depth of the container at a distance of 50% of the container radius. Label and submit each sample for measurement of suspended solids.

5. Repeat two samples at one mixing intensity to determine reproducibility. Label and submit each sample for measurement of suspended solids.

6. Select one sample for larger-scale confirmation testing. Place 40 gallons of dredge slurry simulation in a 55-gallon drum with a variable-speed mixer at known energy consumption.

7. Stir at speeds corresponding to mixing intensity, G, of 200, 500, and 1,000 sec^{-1}. At each speed, acquire one sample from beneath the surface at a depth of 20% of the full water depth of the drum, and at a distance of 50% of the drum radius. Label and submit each sample for measurement of suspended solids.

For each test result calculate c_t/c_o % of fully-mixed (initial) suspended solids concentration. Plot these calculated results vs. velocity gradient, G.

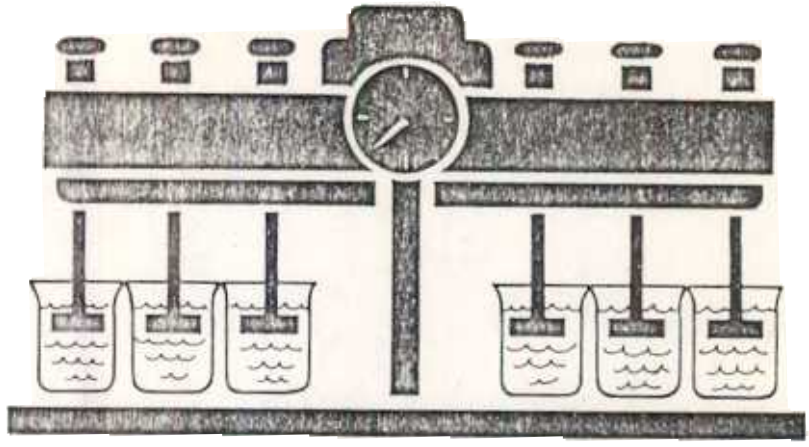
V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Camp, T.R. and P.C. Stein. Velocity Gradient and Internal Work in Fluid Motion. Journal of the Boston Society of Civil Engineers, 30, 219, 1943.

Lai, R. J., H. E. Hudson Jr., and J. E. Singley. October 1975. Velocity Gradient Calibration of Jar-Test Equipment. *American Water Works Association Journal*: 553-557.

Velocity Gradient Calibration of Jar-Test Equipment



Ruey J. Lai, H. E. Hudson Jr., and J. E. Singley

A paper contributed to and selected by the JOURNAL, authored by Ruey J. Lai (Student Member, AWWA), Environmental Sciences & Engineering, Inc., Gainesville, Fla.; H. E. Hudson Jr. (Honorary Member, AWWA), pres., Water & Air Research, Inc. Gainesville, Fla.; and J. E. Singley (Active Member, AWWA), prof., Wtr. Chem., also of the Dept. of Envir. Engrg. Sciences, Univ. of Florida, Gainesville, Fla.

During a study to determine mixing intensity, four groups of jars-test systems were utilized and mean velocity gradient, turbulent gross drag coefficient, and Reynolds and Power numbers were calculated. It was concluded that the same G, or mean velocity gradient, values could be produced by impellers of different shapes as long as projected areas were the same.

The jar-test procedure is widely used to simulate the water-pretreatment process in the laboratory to produce data for process control, yet few carefully controlled jar-test techniques are found in related literature. Jar-testing has depended upon the approach of each investigator.[1-3] However, the interpretation of jar-test data must be founded on unvarying and well-calibrated techniques if they are to be quantitatively meaningful. One of the important variables in the procedure is the mixing intensity, which is related to the rotational speed and the configuration of the agitator as well as the geometry of the mixing vessel.

The purpose of this study was to determine the mixing intensity, expressed as the mean velocity gradient "G," throughout the applicable speed range, using various jar-test configurations. The resulting data should prove useful for application of laboratory data to water-treatment-plant design.

Camp[1] has called attention to the facts that (1) the fluid condition in full-scale plant mixing and flocculation basins is always turbulent, even when G values are relatively low; and (2) at speeds commonly used in jar-test machines, laminar flow conditions may occur. One object of this study was to evaluate the minimum threshold speeds above which turbulence always occurs in jar-testing.

Camp and Stein[4] applied Stokes' theory[6] to relate the total energy input to what they called a root-mean-square velocity gradient G (Stokes' theory states that the velocity gradient equals the square root of energy dissipation at a point, divided by the absolute viscosity of the fluid):

$$\left[G = \frac{du}{dz} = \sqrt{\frac{W}{\mu}} \right] \quad (1)$$

where W = dissipation function = power loss per unit volume of fluid

μ = absolute viscosity of the fluid

The value of W depends upon the geometry of the stators, rotors, and containers and upon the speed of the rotors. Accurate values of W can be determined best by measurement of the torque input to the liquid at various speeds and temperature:

$$\left[W = \frac{2\pi s T}{V} \right] \quad (2)$$

in which s is the measured rotor speed in rps, T is the measured torque input, and V is the liquid volume. Once the torque is determined, the value of W can be calculated.

By extensive experiments with hydrous ferric oxide floc, Camp[1] demonstrated that the floc size and volume concentration may be

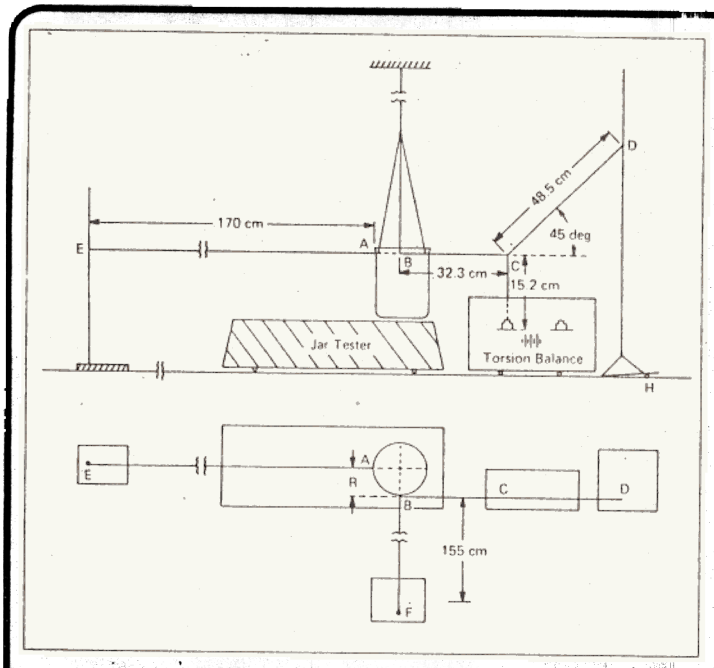


Fig. 1. Torque Measuring Setup

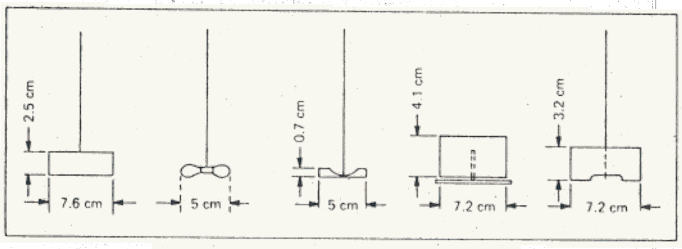


Fig. 2. Sketches of Impellers Tested

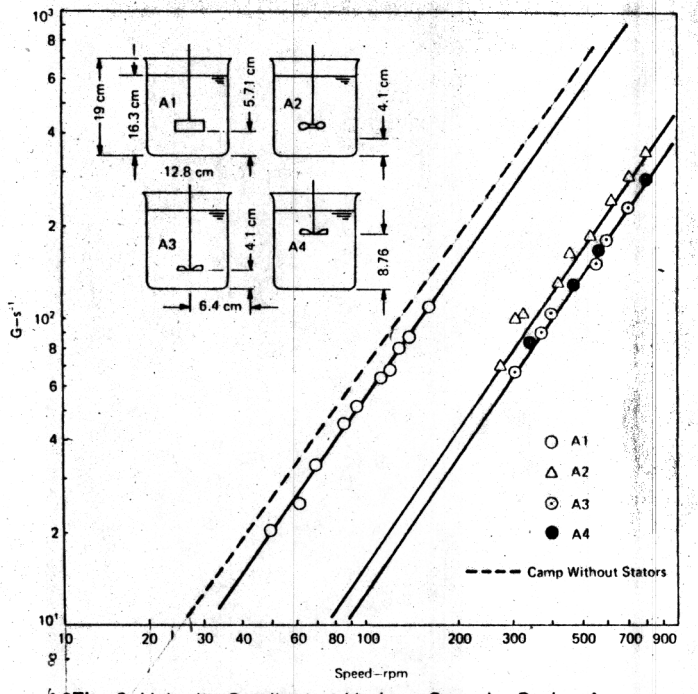


Fig. 3. Velocity Gradient at Various Speeds, Series A

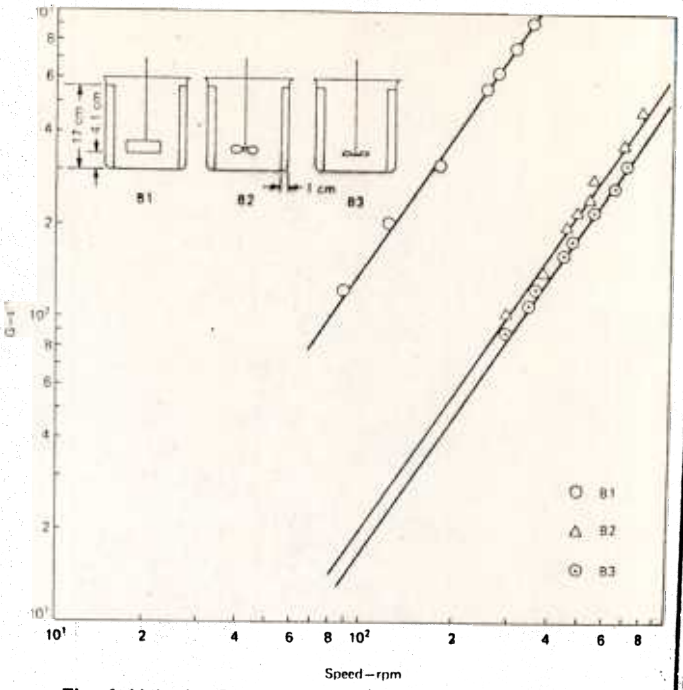


Fig. 4. Velocity Gradients at Various Speeds, Series B

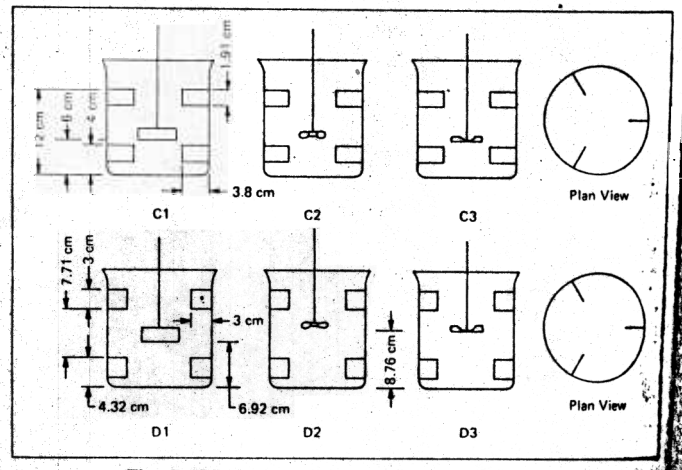


Fig. 5. Configurations Used in Series C and D

TABLE 1
Impeller Characteristics

Blade Type	Diameter, *D*–*cm*	Projected Area, *a*–*cm*²
2-blade paddle*	7.6	17.5
3-blade propeller†	5.0	4.5
2-blade pitched paddle	5.0	2.8
2-blade paddle‡	7.2	28.8
2-blade paddle§	7.2	18.4

*Phipps & Bird, Richmond, Va.
†Marine type
‡Florida 1, Environmental Specialties, Gainesville, Fla.
§Florida 2, Environmental Specialties, Gainesville, Fla.

TABLE 2
Comparison of G Values at 100 rpm

G s⁻¹	Model
140	B-1, C-1, D-1
120	F-1
70	E-1
54	A-1
21	B-2, C-2, D-2
17	B-3, C-3, D-3
16	A-2
13	A-3, A-4

varied over a wide range by changing values of G. The value of G, then, was shown to be an important parameter in coagulation and flocculation processes.

Camp also defined two dimensionless gross drag coefficients in mixing tanks.[8] For fully turbulent flow, the dissipation function $W = 124\,\rho\,a\,C_f s^3$, where 124 is $(2\pi)^3/2$, ρ is the mass density of the liquid, a is the projected area of the rotor blades, and C_f is the turbulent gross drag coefficient determined by the geometry of the system. For laminar flow, $W = 4.92\pi\,C_v s^2$ where 4.92 is $(2\pi)^2/8$ and C_v is the viscous gross drag coefficient determined by the geometry of the system. Since $W = G^2\mu$ in turbulent flow

$$G^2 = K_1 C_f s^3 \tag{3}$$

where

$$K_1 = 124\,\frac{\rho a}{\mu}$$

In laminar flow

$$G^2 = K_2 C_v s^2 \tag{4}$$

where $K_2 = 4.92$

C_f and C_v values can be calculated using G and s values from G vs s diagrams.

Because of the complex fluid motion in a mixing tank, another approach utilizing pure power consumption was developed.[8-10] This approach has been used in the chemical industry. Three dimensionless groups, namely

$$\text{Reynolds number} \quad N_{Re} = \frac{D^2 s \rho}{\mu} \tag{5}$$

$$\text{Froude number} \quad N_{Fr} = \frac{Ds^2}{g} \tag{6}$$

$$\text{Power number} \quad N_p = \frac{P g_c}{\rho s^3 D^5} \tag{7}$$

are useful here. D is impeller diameter, P is power, and g is gravitational acceleration. N_{Re} represents the ratio of inertial forces to gravitational forces. N_p was considered as a drag coefficient or friction factor. For a fully baffled tank, N_{Fr} becomes unimportant and drops out.[9-11] By plotting N_p vs N_{Re} in log-log form, one is able to show the power required to turn an impeller at any speed in any environment.

Experimental Procedures

—The torque measurements were performed using the test setup depicted in Fig. 1. A 2-l beaker was hung by a 0.3-cm-OD copper wire attached to the ceiling. Two long steel wires, 0.05-cm OD, were attached to the beaker at points A and B from points E and F, respectively, in order to keep the beaker from vibrating. A short, thin, strong cotton thread BC, perpendicular to the steel wire BF, was attached to point B. A second thread that formed a 45-deg angle to thread BC was attached to point C at one end and to a stand on the other. The 45-deg angle was convenient for the force balance at point C. During each measurement the angle tended to change slightly because of the tension in the threads. This was corrected by a fine adjusting screw H on the bottom of one side of the stand. The difference between two weights that maintained the balance on the scale pans was the force (in grams) of the torque resulting from the rotation of the rotor. The torque arm, R, was measured between AE and BC and found to be constant at 7.0 cm. The temperature of the water was determined at the time of each torque measurement. The initial force without any rotor rotation was close to zero and was kept constant at 1 g by adjusting the screw H. This value was substracted from every force measured thereafter. Force values measured in this study ranged from 1 to 120 g. The revolution of the rotor was measured by a tachometer at low speed and by a stroboscopic light* at high speed.

Once the torque was measured, W was calculated. From known values for the viscosity of water at the temperature of the experiment and the valve of W, G values were calculated. Values of C_f and C_v were calculated using Eq (3.4). Reynolds numbers and Power numbers were calculated by using Eq (10.7). Note that power P = dissipation function W times the volume of the liquid (2 000 cm³). The model, type, diameter and projected area of blades are shown in Table 1 and Fig. 2.

Results and Discussions

The first setup tested (series A) made use of a 2-l beaker without baffles. The rotors used were a paddle†, a small three-blade marine-type mixing propeller† and small pitched two-blade paddles.† The only other difference was the distance of the paddle from the vessel bottom. The impeller dimensions, distance of impeller above the vessel bottom together with their G values are shown in Fig. 3. All curves had slopes of 3/2 at rpm > 60. It can be seen that the first model had higher G values than either the second or the third. However, the G values were slightly lower than those obtained by Camp[7] (Fig. 1). It was observed also that the distance of the pitched blade, (third and fourth models) above the beaker bottom did not change the G value in the test range for clearances of 4.1 cm and 8.76 cm.

The second configurations tested (series B) involved a beaker with 4 long baffles, 1 cm × 17 cm, extended from top to bottom, separated 90 deg each with a paddle.‡ a propeller.‡ and a pitched paddle.‡ This type of baffling is commonly used in the chemical industry. For the experiment, the baffles were made of acrylic and attached to the beaker with cement (see Fig. 4). Again, the paddle yielded higher values than the pitched-blade impellers. The slopes of the curves were 3/2 in the test range.

The third configurations tested (series c) involved a 2-l beaker with three sets of twin rectangular baffles (3.8 cm × 1.9 cm). The beaker configuration was identical to the one used by Camp[2] (Fig. 1) except for the method of stator attachment. In Camp's experiments the stators were attached to a metal framework and placed in the beaker. This left some void space between stators and the beaker. As in the second configuration, the stators were cemented directly to the beaker.

The fourth configuration tested (series D) used a 2-l beaker with six 3 × 3-cm baffles similar to those used by Camp[2]. Again, the baffles were attached by cementing. Figure 5 shows the dimensions of the systems. Figure 6 shows the G values obtained. The curves had slopes of 3/2 in the test range. The two different shapes of baffles resulted in the G values of all three systems, i.e., C–1 = D–1; C–2 = D–2; C–3 = D–3. However, the G values of C–1 (or D–1) were much higher than that from the other two systems. The data show that the quadruple and triple baffles had the same effect. A comparison of Fig. 4, 6 also reveals that the G values for B–1 in Fig. 4 were the same as D–1 in Fig. 6. This means that the long baffles had the same effect as either the rectangular or square baffles.

The last two setups tested were series E–1 and F–1 which utilized a magnetic-drive jar tester.§ E–1 had no stators, whereas F–1 had three-blade stators.

*STROBOTAC, General Radio Co., Concord, Mass.
†Models A-1, A-2, A-3, A-4, respectively; Phipps & Bird, Richmond, Va.
‡Models B-1, B-2, and B-3, respectively; Phipps & Bird
§Environmental Specialties, a Div. of Water and Air Research, Inc., Gainesville, Fla.

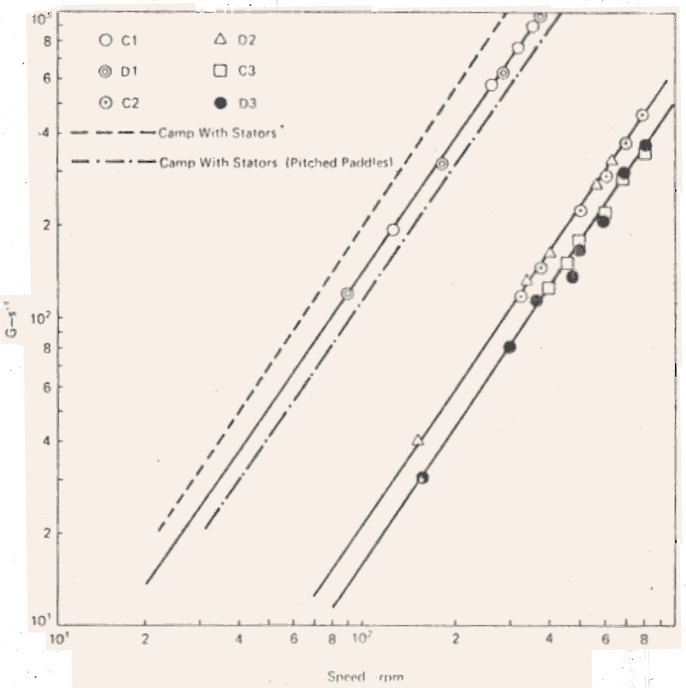


Fig. 6. Speed vs Velocity Gradient, Series C and D

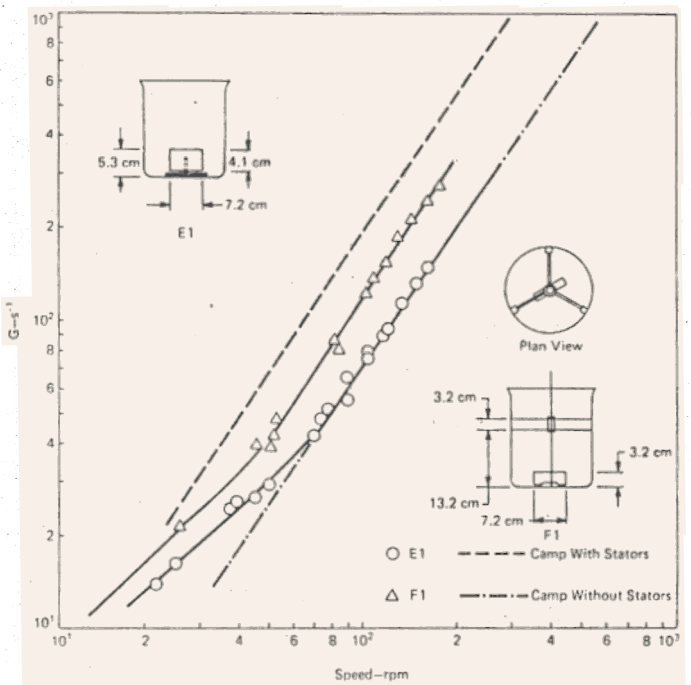


Fig. 7. Calibration of Magnetic Stirring System, Series E and F

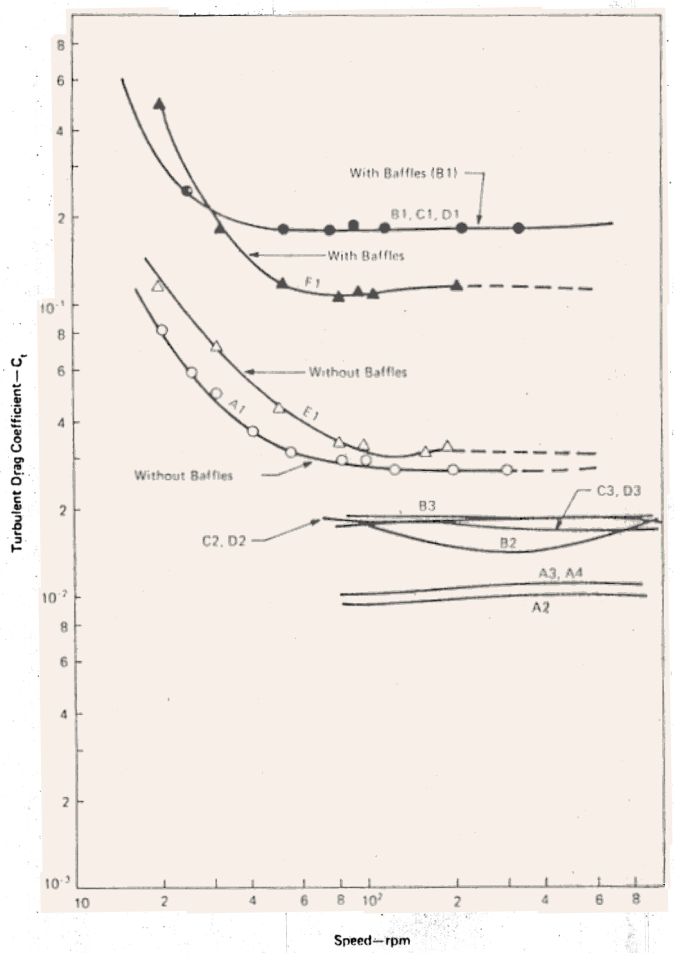


Fig. 8. Turbulent Drag Coefficients for Various Impeller Speeds

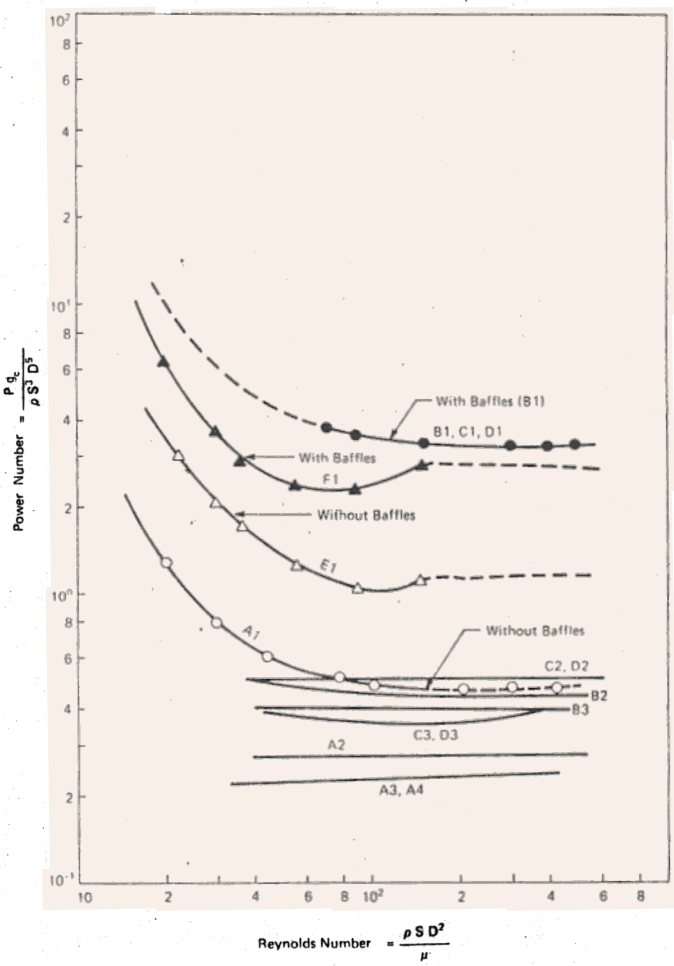


Fig. 9. Impeller Power Correlations

*Phipps & Bird

Figure 7 shows the configuration and G values of these systems. The curves have slopes of 3/2 at higher rpm. For F–1 the slope changed to 1 at 45 rpm and below. For E–1 the point of inflexion occurred at 75 rpm.

Comparison of Fig. 6, 7 reveals that the G values for F–1 were almost as high as B–1. E–1, although it yielded lower G values than F–1, generated more mixing than the small marine type and pitched-blade paddles with baffles. Above 75 rpm E–1 values coincided with Camp's data for paddles without stator.*

For comparison, the G values at 100 rpm for each model have been listed in Table 2.

It is interesting to note that the marine-type propeller and the pitched-blade propellers had the same G for three different baffle configurations.

The C_t results were calculated and are shown in Fig. 8. They were similar in shape to those from Camp's data[1] (Fig. 3-6). C_t was approximately constant in the higher rpm. For each setup, there was a rotational speed below which C_t increased as the speed was decreased. When C_t is constant, from Eq (3)

$$G^2 = K_{11}s^1 \tag{8}$$

where $K_{11} = K_1C_t$, so log G log vs log s has a slope of 3/2.

Figure 8 also shows that the installation of baffles increases the turbulent drag coefficients for various impeller speeds.

Computations of Impeller Characteristics

One may suppose it was desired to find the projected area of a marine-type propeller to achieve the same G values as C–1* (see Fig. 5, 6). From the definition of C_t and the G and W correlations, $G^2\mu = 124\ \rho\ C_t s^3 a$, that is

$$aC_t = \frac{G^2\mu}{124\ \rho s}$$

From Fig. 6 (curve C–1), when rpm = 130, $G = 200\ s^{-1}$, assuming water temperature of 25C so that $\mu = 1cp = 1 \times 10^{-2}$ g cm^{-1} s^{-1} and $\rho = 1$g cm^{-3}, then

$$aC_t = \frac{G^2\mu}{124\ \rho s} = 0.316\ \text{cm}^2$$

Now, since the C_t vs rpm curve for this "unknown" propeller is not available, one may utilize the C–2 and D–2 curve (three-blade marine-type propeller with 4.5 cm^2 projected area). Figure 8 (curve C–2 and D–2) shows that when $s = 130\ \text{min}^{-1} = 13/6\ \text{s}^{-1}$, $C_t = 1.8 \times 10^{-1}$, hence

This value corresponds very closely to the projected area of the paddle,* 17.5 cm (see Table 1). This example verified Camp's conclusion[1] that impellers produce the same mean-velocity gradient G as long as they have the same projected areas.

Energy Input Into the Jar

The energy input at different rotational speeds in mixing is usually expressed by plotting N_{Re} vs N_p. This plot for A–1 and B–1, i.e., C–1 or D–1 (Fig. 9) shows that there is a constant energy increase into the jar because of installation of baffles. Similarly for magnetic-drive jar testers, F–1 had higher energy input than E–1 even though F–1 had a slightly smaller rotor (Fig.). Figure 9 also shows the impeller power correlations for various systems.

*Phipps & Bird

Comparison of N_p and C_t

From definitions of N_p and C_t,

$$N_p = \frac{Pg_c}{\rho s^3 D^5}, \quad C_t = \frac{W}{124\ \rho as} = \frac{P}{124\ \rho as^3 V}$$

it can be shown that

$$\frac{N_p}{C_t} = 124\ \frac{aVg_c}{D^3}$$

Thus the ratio of N_p/C_t, is constant for specific systems. From Fig 8 (C_t vs S), the data plotted in Fig. 9 (N_p vs N_{Re}) can be calculated so that one could compare those particular values with literature values.

Minimum Threshold Speeds

The curves of C_t, illustrated in Fig. 8 are based on fully turbulent drag which is assumed to be proportional to the square of velocity.[1] The proportionality does not hold except where the curves are nearly horizontal.

The minimum threshold speed above which turbulence always results can be seen from Fig. 8 to be, in general, about 100 rpm for each unbaffled system.

For the paddle with baffling,* the minimum is approximately 40-50 rpm and for the other paddle† is about 70-80 rpm with baffles.

Conclusions

Four groups of jars-test systems were studied. The torques were measured as functions of system geometry and rotor velocity. Values for G, C_t, N_{Re}, and N_p were calculated. Although flow patterns may be different, impellers of different shapes produce the same G values as long as their projected areas are the same. This is in agreement with Camp's conclusions.[1] It was observed that variation of the distance of the impellers from the beaker bottom in unbaffled jars did not change the energy input.

The installation of baffles increased the energy input; however, all fully baffled jars have the same energy input regardless of baffle size or geometry with a given size and shape of the impeller.

References

1. Black, A. P., et al. Review of the Jar Test. *Jour. AWWA*. 49:11:1414 (Nov. 1957).
2. Camp, T. R. & Conklin, G. F. Toward a Rational Jar Test For Coagulation. *Jour. NEWWA*. 84:325 (1970).
3. Technique for Laboratory Coagulation Test. Tech. Inquiry Rprt., No. 248 (A). The Water Res. Assn., England (Aug. 1973).
4. Camp, T. R. Hydraulics of Mixing Tanks. *Jour. Boston Soc. Civ. Engrg.*, (Jan. 1969). p. 1.
5. Camp, T. R. & Stein, P. C. Velocity Gradients and Internal Work in Fluid Motion. *Jour. Boston Soc. Civ. Engrg.*, 30:4 (Oct. 1943).
6. Stokes, G. G. On the Theories of Internal Friction of Fluids in Motion, Etc. *Camb. Phil. Trans.*, t. viii (1845).
7. Camp, T. R. Floc Volume Concentration, *Jour. AWWA*. 60:6:656 (Jun. 1968).
8. Rushton, J. H.; Costich, E. W.; & Everett, H. J. *Chem. Engrg. Prog.*, 46:395 (1950).
9. Johnstone, R. E. & Thring, M. W. *Pilot Plants, Models, and Scale-up Methods in Chemical Engineering*. McGraw-Hill Book Co., Inc., New York, N. Y. (1957).
10. Uhl, V. W. & Gray, J. B. Mixing-Theory and Practice. Vol I, Ch. 4. AP, Inc., New York, N. Y. (1966).
11. McCabe, Warren L. & Smith, Julian C. *Unit Operations of Chemical Engineering*. McGraw-Hill Ser. in Chem. Engrg., New York, N. Y. (2nd ed., 1957). p. 258.

*Phipps & Bird
†Florida, Environmental Specialties, Gainesville, Fla.

Appendix 17

SOP – Multimedia Filter Tests

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Multimedia Filter Tests

I. Scope and Application

This standard operating procedure (SOP) describes the procedure for performing Multimedia Filter Tests as part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

Hudson River dredged material may be transported hydraulically to land-based processing facilities, where they would be desanded (particle size separation) and the slurry of finer particulates would be dewatered, likely using a plate and frame filter press, belt press, or centrifuge. The filtrate (or centrate) from the dewatering operations would need additional treatment (water treatment) prior to discharge.

Multimedia filtration would likely be used for additional solids removal following flocculation and gravity settling. Multimedia filters use media of different sizes and densities so that after hydraulic classification (backwashing) they have coarser media above finer media, so solids removals occur deeper in the bed, rather than the top surface, as in single-media filters. A common configuration, used here, is the dual-media filter with anthracite above sand.

The primary objective of water filtration tests is to demonstrate the PCB removals and effluent quality that can be expected following multimedia filtration at typical design loading conditions (2 to 8 gpm/ft^2). Quantities of filter press filtrates will be generated from several hydraulically dredged material simulations to represent the range of PCB concentrations that may be expected during dredging operations.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (BBL, 2003);
- Lexan or glass column, 4-inches diameter x 8-feet high;
- Gravel/coarse sand underdrain;
- Filter sand, 0.45 to 0.55 mm effective size, 24-inch bed depth.
- Anthracite, 1.5 to 2 millimeters (mm) effective size, 24-inch bed depth;
- Feed pump: 0.1 to 1 gallons per minute (gpm) positive displacement;
- Sample containers; and
- Laboratory notebook.

III. Health and Safety Considerations

Refer to the Revised HASP (BBL, 2003).

IV. Multimedia Filter Test Procedure

Procedures for the Pilot Multimedia Filter Test are described below:

1. The filter column will be backwashed to a 2:1 expansion volume before each hydraulically dredged material simulation feed at the three filter loading rates.

2. Each of the settled water samples will be fed at hydraulic loading rates of 2, 6, and 10 gpm per square foot (sq ft). For a 4-inch-diameter column, these loadings are attained at flow rates of 0.17, 0.52, and 0.87 gpm. Check feed rate by volumetric measurement of effluent with timer.

3. Samples of influent and effluent will be obtained after filtration of 10 bed volumes (100 L or 26 gallons) at each hydraulic loading rate.

4. Aliquots of feed and filtered samples will be analyzed for parameters listed in Table 2 of the TS Work Plan.

Note: The principal purpose of these tests is to confirm attainable removal rates for various constituents from a variety of simulated and treated dredge slurries. The run lengths are abbreviated and are not expected to terminate because of headloss. Pressures and headlosses are not monitored. Specific captures of contaminants (pounds per sq. ft. per run) are not calculated.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 18

SOP – Rapid Small-scale Column Tests (Crittenden et al., 1991)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Predicting GAC Performance With Rapid Small-Scale Column Tests

John C. Crittenden, Parimi Sanjay Reddy, Harish Arora, John Trynoski, David W. Hand, David L. Perram, and R. Scott Summers

The rapid small-scale column test (RSSCT) is a scaled-down version of a pilot- or full-scale granular activated carbon (GAC) column. Simple equations for selecting the design and operating parameters of RSSCTs from the full-scale process design variables are presented, and their limitations are discussed. Carbon usage rates and breakthrough profiles for RSSCTs are compared with pilot-column results. Case studies representing high and low levels of synthetic organic chemicals, in the presence and absence of background dissolved organic carbon (DOC), and weakly and strongly adsorbing organics are reviewed. For DOC removal, RSSCT and pilot performances were compared for five surface waters and one groundwater.

The design of full-scale granular activated carbon (GAC) adsorption processes can involve time-consuming and expensive pilot-plant studies. To circumvent this problem, rapid methods for the design of large-scale fixed-bed adsorbers from small columns have been examined.[1-6] Frick[1] and Crittenden et al[4,5] have developed and tested scaling equations for designing small columns known as rapid small-scale column tests (RSSCTs), which do not require the use of complicated models but are based on fixed-bed mass transfer models. In the RSSCT method, mass transfer models are utilized to scale down the full-scale adsorber to a small column. Similarity of operation to that of large-scale adsorbers is assured by properly selecting the particle size, hydraulic loading, and empty bed contact time (EBCT) of the small adsorber.

The three primary advantages in using the RSSCT for design are (1) an RSSCT may be conducted in a fraction of the time that is required to conduct pilot studies; (2) unlike predictive mathematical models, extensive isotherm or kinetic studies are not required to obtain a full-scale performance prediction from an RSSCT; and (3) a small volume of water is required for the test, which can be transported to a central laboratory for evaluation. Although replacing a pilot study with an RSSCT significantly reduces the time and cost of a full-scale design, the limitations of RSSCTs must be recognized. The purpose of this article is to examine those limitations by comparing RSSCT effluent profiles to pilot data for both synthetic organic chemicals (SOCs) that are targeted for removal and dissolved organic carbon (DOC).

Selecting operational parameters for RSSCT

The development of the RSSCT method is discussed in detail by Berrigan[7] and Crittenden et al.[4,5] The selection of the hydraulic loading and EBCT of the RSSCT is determined by considering those mechanisms that cause spreading in the mass transfer zone and breakthrough curve: (1) external mass transfer resistance or film transfer, (2) axial mixing resulting from dispersion, and (3) the internal mass transfer resistances of pore and surface diffusion. As far as spreading of the breakthrough curve is concerned, internal mass transfer resistance is usually more important than external mass transfer resistance for large molecules (>300 MW) and equally important for small molecules (approximately 100–200 MW). However, the interaction of small molecules and background organic matter (such as humic substances) can cause internal mass transfer, in some cases, to be the most important spreading mechanism for small molecules. Dispersion is usually negligible if the hydraulic loading is high enough.

The EBCT of the RSSCT, $EBCT_{SC}$, is determined from intraparticle mass transfer resistances. If the dependence of the pore and surface diffusion coefficient on particle size is known, similarity may be achieved by equating the dimensionless groups that consider the intraparticle diffusion resistances in the small and large columns. If the void fractions, bulk densities, and capacities are identical for the carbons that are used in the RSSCT and full-scale process, the proper scaling between the small-and large-column EBCTs can be determined from this equation:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{2-X} = \frac{t_{SC}}{t_{LC}} \qquad (1)$$

in which $EBCT_{SC}$ and $EBCT_{LC}$ are the EBCTs of the small and large columns; $d_{p,SC}$ and $d_{p,LC}$ are the adsorbent particle sizes for the small and the large GAC; and t_{SC} *and* t_{LC} are the corresponding elapsed times in the small- and large-column tests, respectively. In the following equations, X defines the dependence of the intraparticle diffusion coefficient on particle size. For surface diffusion control, X is given by the expression:

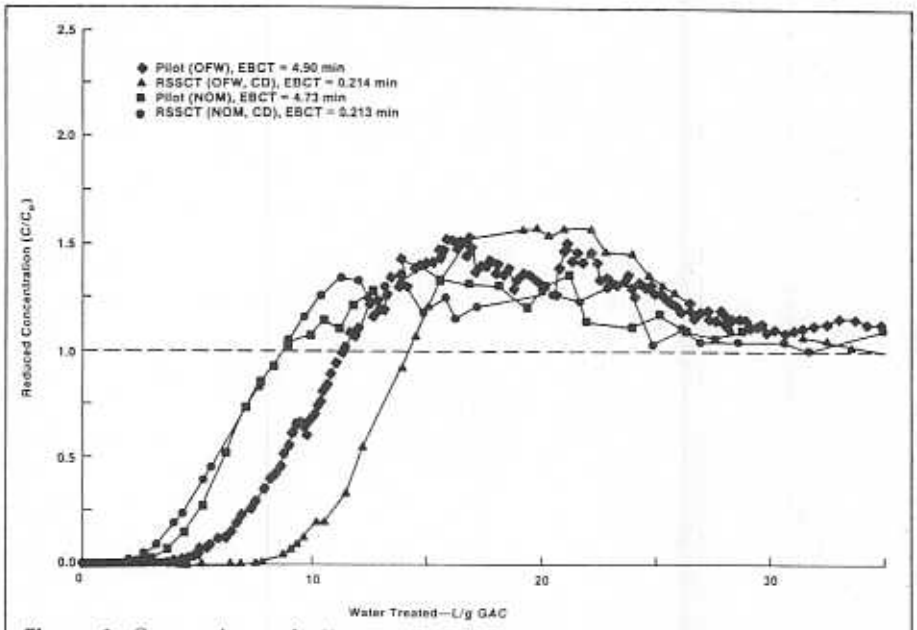


Figure 1. Comparison of pilot-column and CD-RSSCT effluent concentration profiles for chloroform in ultrapure water and surface water (*pilot particle size—0.1026 cm; RSSCT particle size—0.0212 cm*)

A full report of this project (catalog no. 90549) is available from the AWWA Research Foundation, 6666 W. Quincy Ave., Denver, CO 80235.

TABLE 1

Results of RSSCT and pilot studies of synthetic organic chemicals targeted for removal

Study Number	Reference and Water Source	Target Compounds Removed	Pilot Influent Concentration *mg/L*	RSSCT Influent Concentration *mg/L*	RSSCT Design	Pilot EBCT *min*	RSSCT EBCT *s*	Pilot Loading Rate *m/h*	RSSCT Loading Rate *m/h*	Pilot Column Capacity *mg/g*	RSSCT Column Capacity *mg/g*	Comments
1	Crittenden et al;[4] distilled and GAC-treated water; Mich. Technol. Univ., Houghton; DOC = 0.2 mg/L	Chloroform	2.609	2.670	CD	1.0	2.5	5.0	24.4			Excellent comparisons between the CD-RSSCT and pilot-column effluent profiles were observed for each component. Both the RSSCT and the pilot column profiles were film transfer-controlled. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.0212 cm.
		TCE	3.397	2.763								
		DBCM	5.367	5.293								
		EDB	5.730	5.845								
		Bromoform	4.366	4.731								
		PCE	2.281	3.018								
2	This study; distilled and GAC-treated water; Mich. Technol. Univ., Houghton; DOC = 0.2 mg/L	Chloroform	1.021	0.981	CD	4.9	12.8	5.1	24.9	8.75	10.24	Good comparisons between CD-RSSCT and pilot-column effluent concentration profiles were observed. The pilot column and RSSCT had approximately equal intraparticle and external mass transfer resistances. The RSSCT effluent concentration profiles appeared slightly later than the pilot-column effluent concentration profiles, and the deviation increased as adsorbability of the compound and EBCT increased. GAC particle sizes: Pilot = 0.1026 cm, RSSCT = 0.0212 cm.
		DBCM	1.775	1.839						34.81	41.33	
		EDB	1.577	1.692						34.70	33.95	
		Bromoform	2.111	2.191						69.95	73.74	
		TCE	1.062	1.201						35.27	37.63*	
		PCE	1.139	1.345						79.70†	98.21†	
3	This study; distilled and GAC-treated water; Mich. Technol. Univ., Houghton; DOC = 0.2 mg/L	Chloroform	1.021	0.981	CD	9.6	25.6	5.1	24.9	10.51	9.30	
		DBCM	1.775	1.839						35.21	44.22	
		EDB	1.577	1.692						34.44	35.27	
		Bromoform	2.111	2.191						76.69*	78.08*	
		TCE	1.062	1.201						32.92†	40.83†	
		PCE	1.139	1.345						78.46†	146.02†	
4	This study; distilled and GAC-treated water; Mich. Technol. Univ., Houghton; DOC = 0.2 mg/L	Chloroform	1.021	1.019	CD	4.9	4.3	5.1	40.2	8.75	1.86	The CD-RSSCT breakthrough appeared much earlier than the pilot breakthrough. This could have been caused by the high pressure drop and channeling or much slower kinetics for the GAC that was used in the RSSCT. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.013 cm.
		DBCM	1.775	1.849						34.82	26.81	
		EDB	1.577	1.528						34.70	22.54	
		Bromoform	2.111	2.002						69.84	47.05*	
		TCE	1.062	1.073						39.18*	30.30*	
		PCE	1.139	1.189						79.70†	37.40†	
5	This study; distilled and GAC-treated water; Mich. Technol. Univ., Houghton; DOC = 0.2 mg/L	Chloroform	1.021	1.019	CD	9.6	8.8	5.1	40.2	10.51	7.72	
		DBCM	1.775	1.849						35.21	24.85*	
		EDB	1.577	1.528						34.44	32.09*	
		Bromoform	2.111	2.002						76.69*	33.73†	
		TCE	1.062	1.073						32.92†	27.61†	
		PCE	1.139	1.189						78.46†	20.31†	
6	This study; surface water; Portage Lake; Houghton, Mich.	Chloroform	0.931	0.943	CD	4.8	12.8	5.2	23.9	5.66	5.72	The CD RSSCT simulated the pilot breakthrough profiles accurately. However, the RSSCT breakthrough appeared after the pilot at longer EBCTs and for better-adsorbed compounds. Pilot-column TOC or NOM breakthrough curves were not predicted from RSSCT profiles. NOM had no impact on the kinetics of the SOC, but a loss of capacity was observed. GAC particle sizes: pilot = 0.1026 cm, RSST = 0.0212 cm.
		DBCM	1.615	1.714						21.45	22.31	
		EDB	1.409	1.549						21.07	24.04	
		Bromoform	1.821	1.948						36.35	43.10*	
		TCE	0.875	1.022						20.32*	27.39*	
		PCE	0.995	1.372						28.27†	41.71†	
		NPDOC	3.560	5.260						0.3070‡	0.2300‡	
7	This study; surface water; Portage Lake, Houghton, Mich.	Chloroform	0.931	0.943	CD1	9.8	26.1	5.2	23.9	5.93	6.23	
		DBCM	1.615	1.714						20.07	24.42*	
		EDB	1.409	1.549						18.96*	23.30†	
		Bromoform	1.821	1.948						26.54†	29.81†	
		TCE	0.875	1.022						13.09†	15.76†	
		PCE	0.995	1.372						14.99†	21.10†	
		NPDOC	3.560	5.260						0.4940‡	0.3750‡	

TABLE 1, continued

Results of RSSCT and pilot studies of synthetic organic chemicals targeted for removal

Study Number	Reference and Water Source	Target Compounds Removed	Pilot Influent Concentration *mg/L*	RSSCT Influent Concentration *mg/L*	RSSCT Design	Pilot EBCT *min*	RSSCT EBCT *s*	Pilot Loading Rate *m/h*	RSSCT Loading Rate *m/h*	Pilot Column Capacity *mg/g*	RSSCT Column Capacity *mg/g*	Comments
8	This study; surface water; Portage Lake, Houghton, Mich.	Chloroform	0.931	0.999	PD	4.8	56.9	5.2	4.9	5.66	9.42	The kinetics of the PD RSSCT were much faster than those of the pilot plant because external mass transfer resistance was important, and the PD design reduces the effect of external mass transfer resistance. Because the SOC concentrations were high, NOM had no impact on intraparticle mass transfer of the SOCs. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.0212 cm.
		DBCM	1.615	1.647						21.45	13.76	
		EDB	1.409	1.509						21.07	16.52	
		Bromoform	1.821	1.977						36.35	43.29*	
		TCE	0.875	1.026						20.32*	29.23*	
		PCE	0.995	1.113						28.27†	33.80†	
		NPDOC	3.560	4.140						0.3070‡	0.2960‡	
9	This study; surface water; Portage Lake, Houghton, Mich.	Chloroform	0.931	0.999	PD	9.8	114.7	5.2	4.9	5.93	10.48	
		DBCM	1.615	1.647						20.07	14.97*	
		EDB	1.409	1.509						19.57	14.09†	
		Bromoform	1.821	1.977						26.54†	18.52†	
		TCE	0.875	1.026						13.09†	9.58†	
		PCE	0.995	1.113						14.99†	10.47†	
		NPDOC	3.560	4.140						0.4940‡	0.5130‡	
10	Crittenden et al;[7] groundwater; Wausau, Wis.; untreated, DOC = 8.35 mg/L	DCE	0.081	0.109	CD	1.0	2.5	4.6	24.4	2.82	2.37	The three CD RSSCTs showed less capacity than the pilot columns. The observed influent concentrations of the RSSCTs were much lower than those observed during the pilot-column study. Vinyl chloride, ethyl benzene, and *o,m,p*-xylenes were present in trace quantities. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.0212 cm.
		TCE	0.067	0.076						5.65	4.60	
		PCE	0.045	0.056						12.50	5.31	
		Toluene	0.022	0.025						11.80§	3.13	
11	Crittenden et al;[7] groundwater; Wausau, Wis.; untreated, DOC = 8.35 mg/L	DCE	0.081	0.069	CD	3.2	9.5	4.6	19.2	0.75	1.78	
		TCE	0.067	0.045						6.13	2.31	
		PCE	0.045	0.033						5.72§	1.80	
		Toluene	0.022	0.012						2.65§	0.61	
12	Crittenden et al;[7] groundwater; Wausau, Wis.; untreated, DOC = 8.35 mg/L	DCE	0.081	0.069	CD	5.4	12.2	4.6	22.7	4.27	1.54	
		TCE	0.067	0.033						5.55§	1.15	
		PCE	0.045	0.026						3.84§	0.88	
		Toluene	0.022	0.016						1.23§	0.70	
13	Crittenden et al;[7] groundwater; Wausau, Wis.; untreated, DOC = 8.35 mg/L	DCE	0.081	0.069	PD	1.0	12.2	4.6	22.7	2.82	1.54	Good comparisons between the PD-RSSCT and pilot-column effluent profiles were observed. The PD RSSCT showed similar capacity and kinetics. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.0212 cm.
		TCE	0.067	0.033						5.65	1.15	
		PCE	0.045	0.026						12.50	0.88	
		Toluene	0.022	0.016						11.80§	0.70	
14	Hineline et al;[9] groundwater, Suffolk County, N.Y., filtered, DOC = 1-2 mg/L	DCP	0.022	0.018	CD	4.9	5.2	8.8	65.9	0.79	0.90§	Fair similarities between the CD RSSCT and the pilot columns were observed. However, the RSSCT influent concentrations were lower than those observed for the pilot columns. When the influent concentrations to the RSSCTs were similar to those observed in the pilot columns, then the RSSCT profiles were in agreement with the pilot-column profiles. GAC particle size: pilot = 0.161 cm, RSSCT = 0.212 cm.
		Aldicarb sulfoxide	0.022	0.012						1.14	0.66§	
		Aldicarb sulfone	0.029	0.014						1.46	0.56	
		TCP	0.011	0.006								
		Carbofuran	0.009	0.004								
15	Hineline et al;[9] groundwater; Suffolk County, N.Y., filtered, DOC = 1-2 mg/L	DCP	0.018	0.014	CD	4.9	5.2	8.8	65.9	1.11	0.92§	
		Aldicarb sulfoxide	0.013	0.008						1.06	0.61§	
		Aldicarb sulfone	0.017	0.012						1.34	0.72§	
		TCP	0.005	0.003								
		Carbofuran	0.003	0.003								
16	Hineline et al;[9] groundwater; Suffolk County, N.Y., filtered, DOC = 1-2 mg/L	DCP	0.015	0.010	CD	4.9	5.2	8.8	65.9	0.76	0.88§	
		Aldicarb sulfoxide	0.008	0.008						0.63	0.54§	
		Aldicarb sulfone	0.011	0.009						0.80	0.73§	
		TCP	0.003	0.002								
		Carbofuran	0.002	0.001								

TABLE 1, continued

Results of RSSCT and pilot studies of synthetic organic chemicals targeted for removal

Study Number	Reference and Water Source	Target Compounds Removed	Pilot Influent Concentration *mg/L*	RSSCT Influent Concentration *mg/L*	RSSCT Design	Pilot EBCT *min*	RSSCT EBCT *s*	Pilot Loading Rate *m/h*	RSSCT Loading Rate *m/h*	Pilot Column Capacity *mg/g*	RSSCT Column Capacity *mg/g*	Comments
17	Summers et al;[10] Rhine River water, Karlsruhe, FRG, water treated by flocculation and filtration, DOC = 2.25 mg/L	TCE	0.31	1.31	CD	6.0	5.7	10.0	81.8	16.0	25.0	CD RSSCT showed more capacity and slower kinetics compared with the pilot column. Diameter of GAC particles: pilot = 0.18 cm, RSSCT = 0.022 cm.
18	Summers et al;[10] Rhine River water, Karlsruhe, FRG, water treated by flocculation and filtration, DOC = 2.25 mg/L	TCE	0.31	1.31	PD	1.5	18.3	10.0	52.9	16.0	24.0	CD RSSCT showed similar kinetics but more capacity compared with the pilot column. Diameter of GAC particles: pilot = 0.18 cm, RSSCT = 0.034 cm.
19	Speth and Miltner;[11] groundwater; Greater Miami Aquifer, S.W. Ohio, DOC = 2.6 mg/L	1,2-Dichloroethene	367 367	350 408	CD CD	7.95 7.95	4.2 4.2	10 10	82 82	5.15 5.15	6.21 7.11	CD RSSCT had 20–40 percent more adsorption capacity, and therefore the RSSCT breakthrough appeared after the pilot breakthrough. GAC sizes: pilot = 0.1026 cm, RSSCT =0.00523 cm.
20	Speth;[15] groundwater; Greater Miami Aquifer, S.W. Ohio, DOC = 2.6 mg/L	1,2-Dichloroethene	384 384 384	388 395 395	CD CD CD	1.83 1.83 1.83	1.26 1.26 1.26	9.4 9.3 9.2	77 77 78	6.61 4.01 2.76	7.22 4.56 3.94	Pilot runs were with GAC exposed to NOM for 0, 4, and 16 weeks, whereas CD RSSCT GAC was exposed for 0, 8, and 32 h. RSSCT had 10–37 percent more adsorption capacity and there was a later breakthrough in all columns. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.00523 cm.
21	Niehaus et al;[13] groundwater; Houghton city tap water, DOC = 1 mg/L.	Methylene blue Methylene Blue	40 40	40 40	CD CD	4.63 2.32	5.28 10.56	5.0 5.0	24.4 24.4			The CD RSSCT effluent appeared before the pilot data, which indicates the CD RSSCT does not describe the data for this large molecule. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.0212 cm.
22	Trynoski;[12] surface water; Portage Lake, Houghton, Mich.	Chloroform DBCM EDB Bromoform TCE PCE NPDOC Chloroform DBCM EDB Bromoform TCE PCE NPDOC	0.931 1.651 1.409 1.821 0.875 0.995 3.56 0.931 1.615 1.409 1.821 0.875 0.995 3.560	0.955 1.77 1.510 1.804 1.064 1.332 1.90 0.963 1.790 1.527 1.813 1.085 1.365 2.00	CD2 CD-mix 	9.8	27	5.2	24.9	5.93 20.07 19.57 26.54† 13.09† 14.99† 5.93 20.07 19.57 26.54† 13.09† 14.99†	6.99 29.50 29.02 48.16 35.05 34.62 7.821 30.72 28.42 48.53 33.30 35.50	CD-2 is nearly identical to CD-1 in case study 7. The lower DOC background concentration for CD-2 yields a later breakthrough. GAC particles sizes: pilot = 0.1026 cm, RSSCT = 0.212 cm. CD-mix is a mixture of particle sizes that yield an equivalent uniformity coefficient to the GAC used in the pilot plant. CD-mix gives identical results as the uniform size RSSCT, CD-2. GAC particle sizes: pilot = 0.1026 cm, RSSCT = 0.0264 cm.

*The column capacity was determined by extrapolating the effluent concentration profiles.
†The column capacity was determined by extrapolating the effluent concentration profiles; however, the profiles were too short to extrapolate with precision.
‡Capacity reported as mass of nonpurgeable DOC adsorbed/mass nonpurgeable DOC fed
§This does not represent the true column capacity because the effluent concentration history profiles have not reached their influent concentration.

TABLE 2

Results of RSSCT and pilot studies using DOC to measure adsorption of background organic matter

Reference and Water Source	Target Compound	Influent Concentration (C_o)—mg/L		RSSCT Design	EBCT		Loading Rate (V) m/h		Comments
		Pilot	RSSCT		Pilot min	RSSCT s	Pilot	RSSCT	
Summers et al;[10] Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.72	8.93	CD	4.5	30.0	9.3	30.3	The CD RSSCT effluent profiles appeared before the pilot-plant effluent profiles. Diameter of GAC particles: pilot = 0.085 cm, RSSCT = 0.026 cm.
	Humic substances	8.72	8.93	CD	8.4	50.0	9.3	30.3	
Summers et al;[10] Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.72	CD	15.6	272.1	5.0	9.3	The CD RSSCT effluent profiles appeared before the pilot-plant effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.085 cm.
	Humic substances	8.03	8.72	CD	28.2	505.4	5.0	9.3	
Summers et al;[10] Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.93	CD	15.6	30.0	5.0	30.3	The CD RSSCT effluent profiles appeared before the pilot-plant effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.026 cm.
	Humic substances	8.03	8.93	CD	28.2	50.0	5.0	30.3	
Summers et al;[10] Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.72	8.93	PD	1.6	30.9	9.3	30.3	The PD RSSCT effluent profiles adequately predicted the large-column effluent profiles. Diameter of GAC particles: pilot = 0.085 cm, RSSCT = 0.026 cm.
	Humic substances	8.72	8.93	PD	2.7	50.0	9.3	30.3	
Summers et al;[10] Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.93	PD	3.0	30.9	5.0	30.3	The PD RSSCT effluent profiles adequately predicted the large-column effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.026 cm.
	Humic substances								
Summers et al;[10] Fuhrberg humic substances in tap water preadsorbed by GAC	Humic substances	8.03	8.72	PD	3.0	97.3	5.0	9.3	The PD RSSCT effluent profiles adequately predicted the large-column effluent profiles. Diameter of GAC particles: pilot = 0.158 cm, RSSCT = 0.085 cm.
	Humic substances	8.03	8.72	PD	15.6	505.4	5.0	9.3	
Wallace et al;[15] Colorado River water, LaVerne, Calif., coagulated and filtered, pretreated with ClO_2	DOC	2.64	2.33	CD	15.0	30.0	1.2	6.6	The CD RSSCT effluent profile appeared before that of the pilot column. The PD RSSCT effluent profiles adequately predicted the pilot-column profiles. As EBCT increased, the RSSCT effluent profiles appeared after the pilot-plant profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
	DOC	2.64	2.22	PD	15.0	165.9	1.2	2.9	
	DOC	2.64	2.11	PD	30.0	331.8	1.2	2.3	
	DOC	2.64	2.09	PD	60.0	662.4	1.2	1.7	
Wallace et al;[15] State project water, LaVerne, Calif., coagulated and filtered, pretreated with ClO_2	DOC	2.64	2.24	PD	15.0	165.9	1.2	1.7	The PD RSSCT effluent profiles predicted the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT =0.021 cm.
Wallace et al;[15] Ohio River water, Cincinnati, Ohio, coagulated and filtered prior to disinfection with chlorine	DOC	2.00	2.17	PD	15.0	165.9		2.9	A good comparison was obtained between the PD RSSCT and the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
Wallace et al;[15] Mississippi River water, Jefferson Parish Water District, La., coagulated and filtered prior to disinfection with chlorine	DOC	2.69	2.69	PD	20.0	165.9		1.7	A good comparison was obtained between the PD RSSCT and the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.
Wallace et al;[15] Delaware River water, Philadelphia Water Department, coagulated and filtered prior to disinfection with chlorine dioxide	DOC	2.72	2.72	PD	15.0	165.9		1.7	A good comparison was obtained between the PD RSSCT and the pilot-column effluent profiles. Diameter of GAC particles: pilot = 0.103 cm, RSSCT = 0.021 cm.

$$\frac{D_{s,SC}}{D_{s,LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^X \quad (2)$$

in which $D_{s,SC}$ and $D_{s,LC}$ are the surface diffusivities of the GAC in the RSSCT and large column, respectively. For pore diffusion control, X is given by:

$$\frac{D_{p,SC}}{D_{p,LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^X \quad (3)$$

in which $D_{p,SC}$ and $D_{p,LC}$ are the pore diffusivities of the GAC in the RSSCT and large column, respectively.

The bed life, bed volumes fed, carbon usage rate, and volume of water that may be treated per mass of carbon (this is termed the specific volume) for the full-scale adsorber can be determined from the RSSCT bed life. For the purposes of this discussion, the RSSCT bed life is simply equal to the allowable run time of the RSSCT before the treatment objective is exceeded. The corresponding bed life for the full-scale column is related to the RSSCT bed life by Eq 1. The bed volumes that can be treated in the full-scale column are equal to the bed life of the RSSCT divided by $EBCT_{SC}$. The specific throughput of the full-scale process is equal to the volume of water fed to the RSSCT divided by the mass of GAC in the RSSCT. The volume of water treated is equal to the bed life of the RSSCT times the flow rate to the RSSCT. The carbon usage rate is the reciprocal of the specific throughput. When evaluating GAC performance, it is important to use bed volumes fed, carbon usage rate, or specific throughput—and not bed life—because the other parameters normalize the results with respect to bed size. Moreover, the value of X does not have an impact on normalized parameters such as specific throughput; it only relates $EBCT_{LC}$ to $EBCT_{SC}$ and determines the run time of the RSSCT.

Constant diffusivity. If it is assumed that the intraparticle diffusivities do not change with particle size ($X = 0$), then exact similarity between RSSCT and pilot-plant effluent profiles can be maintained. The following equation assures that the amounts of spreading caused by intraparticle mass transfer resistances in the RSSCT and pilot plant are identical in relation to adsorber length.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^2 = \frac{t_{SC}}{t_{LC}} \quad (4)$$

If the Reynolds numbers for the small- and large-carbon particles are set equal, an equal amount of spreading in the mass transfer zone caused by external mass transfer and dispersion in relation to the adsorber length can be assured. This gives the following equation:

$$\frac{V_{SC}}{V_{LC}} = \frac{d_{p,LC}}{d_{p,LC}} \quad (5)$$

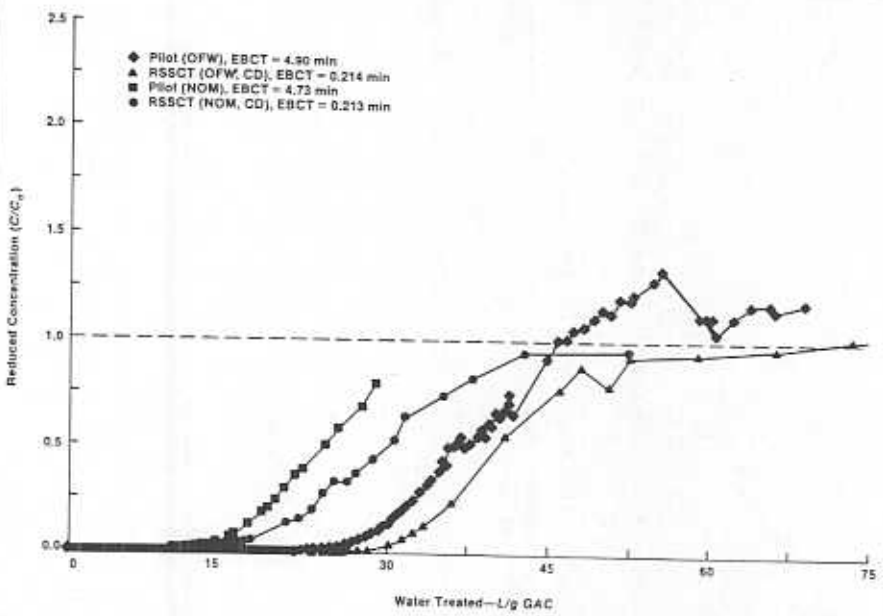


Figure 2. Comparison of pilot-column and CD-RSSCT effluent concentration profiles for trichloroethene in ultrapure water and surface water (*pilot particle size—0.1026 cm; RSSCT particle size—0.0212 cm*)

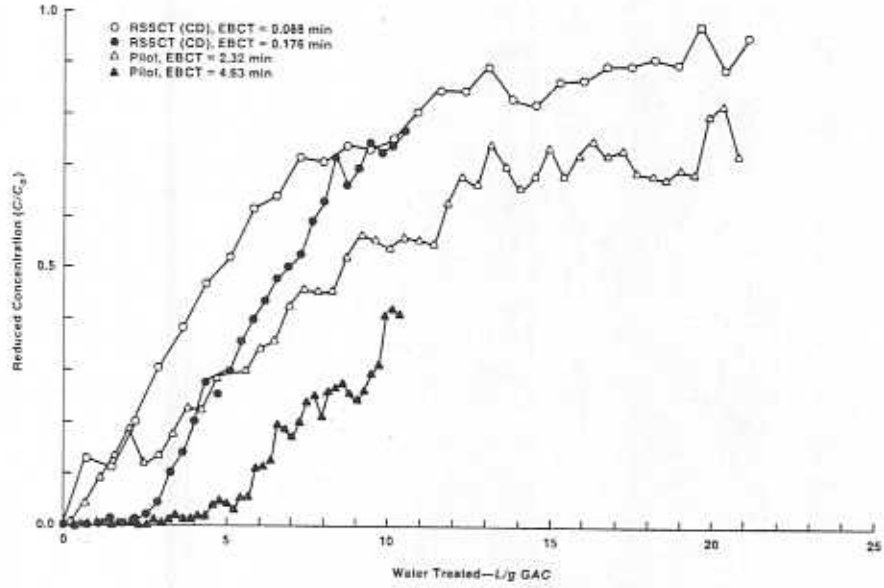


Figure 4. Comparison of CD-RSSCT and pilot-column effluent concentration profiles for methylene blue spiked into Houghton, Mich., groundwater (*the RSSCTs were designed to simulate pilot columns with EBCTs of 2.32 and 4.63 min;*[13] *pilot particle size—0.1026 cm; RSSCT particle size—0.0212 cm*)

in which V_{SC} and V_{LC} are hydraulic loadings in the RSSCT and pilot columns, respectively.

Proportional diffusivity. If intraparticle diffusion causes most of the spreading in the mass transfer zone and the intraparticle diffusivity is proportional to particle size ($X = 1$), the RSSCT's design parameters can be selected using the following equations. The amounts of spreading in the mass transfer zones of the RSSCTs and pilot columns caused by intraparticle diffusion resistances—in relation to their respective column lengths—are identical if this equation is used to determine $EBCT_{SC}$:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right] = \frac{t_{SC}}{t_{LC}} \quad (6)$$

On the other hand, a similar amount of spreading resulting from dispersion and external mass transfer cannot be maintained between RSSCTs and pilot columns. Because intraparticle diffusion resistance usually causes most of the spreading in the mass transfer zone, the amount of spreading caused by disper-

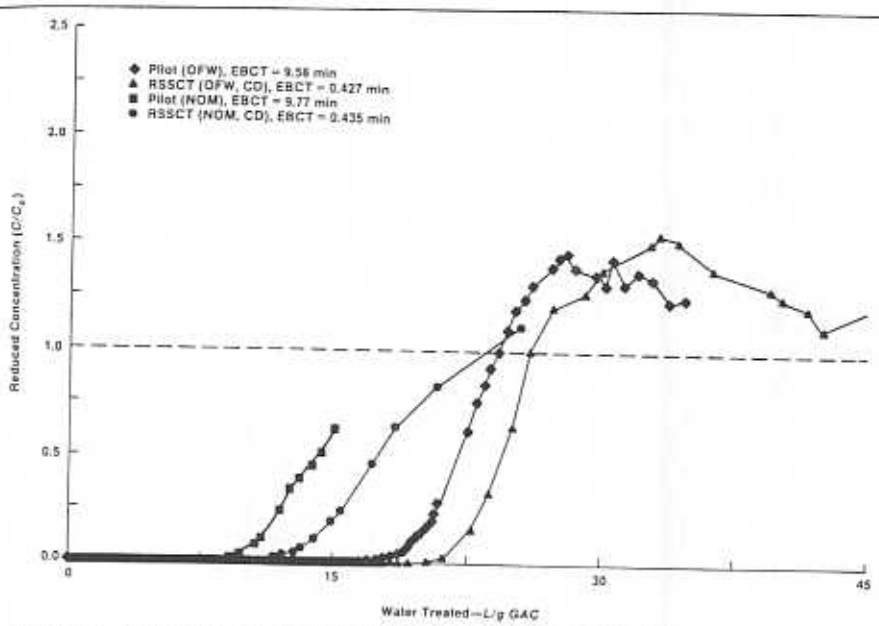


Figure 3. Comparison of pilot-column and CD-RSSCT effluent concentration profiles for 1,2-dibromoethane in ultrapure water and surface water (*pilot particle size—0.1026 cm; RSSCT particle size—0.0212 cm*)

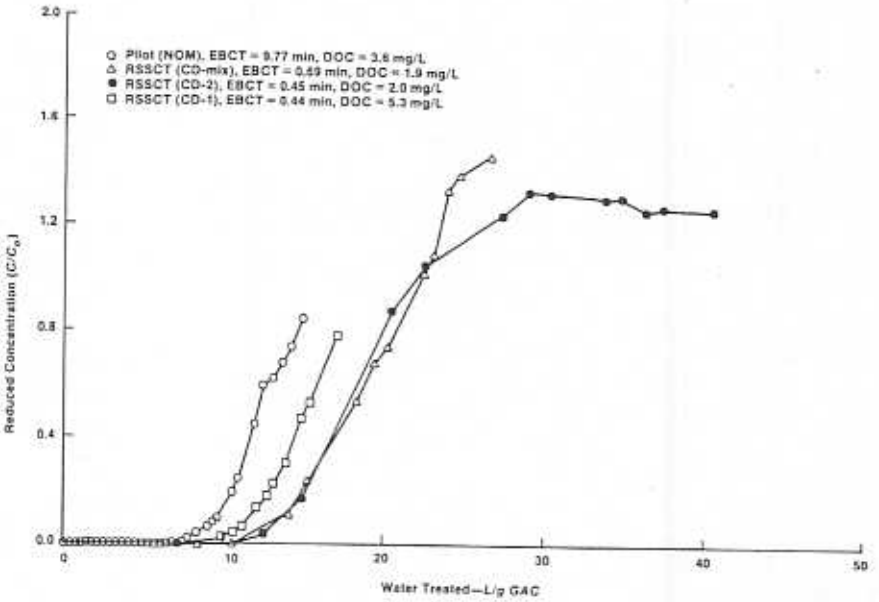


Figure 5. Comparison of CD-RSSCT and pilot-column effluent concentration profiles for 1,2-dibromoethane in Portage Lake water (*all RSSCTs were designed to simulate a pilot column with an EBCT of about 10 min; CD-1 is the 60 × 80-mesh RSSCT, and CD-mix is the mixed-particle-size RSSCT conducted by Trynoski;*[12] *pilot particle size—0.1026 cm; CD-1 and CD-2 particle size—0.0212 cm; CD-mix particle size—0.0264 cm*)

sion and external mass transfer can be reduced in the selection of the RSSCT hydraulic loading without affecting the RSSCT results.

Equation 5 may be used to select the hydraulic loading of the RSSCT. However, in order to reduce the pressure drop and RSSCT column length, Crittenden and co-workers[5] proposed the following equation:

$$\frac{V_{SC}}{V_{LC}} = \frac{d_{p,LC}}{d_{p,SC}} \cdot \frac{Re_{SC,min}}{Re_{LC}} \qquad (7)$$

in which $Re_{SC,min}$ is the minimum Reynolds number that guarantees the effects of dispersion and external mass transfer will not be greater in the RSSCT than in the large column. A value of 1 for $Re_{SC,min}$ usually yields good results, but lower values may be used if head loss and column length are unacceptable.[5]

Experimental materials and methods

The minimum column-diameter-to-particle-size ratio should be 50 to avoid channeling.[8] If large sample volumes are required, larger-diameter columns can be used. For the pilot study 50-mm-ID glass columns were used, and for the RSSCTs 11-mm-ID columns were used.

Preparation of the GAC is very important because a representative sample is required for good results. Representative samples of GAC, which were used in the pilot-scale or large column, GAC_{LC}, were obtained by mixing and splitting. The smaller-size GAC used in the RSSCT studies, GAC_{SC}, was obtained by crushing a representative sample of GAC_{LC}. To obtain GAC_{SC}, a GAC_{LC} sample is crushed until all the GAC_{LC} sample passes through the largest sieve that is used to obtain GAC_{SC}. The GAC_{LC} was crushed carefully to minimize the generation of carbon fines. Yields of approximately 40 and 34 percent by weight were obtained for 60 × 80- and 100 × 140-mesh carbon, respectively. Before startup of the RSSCT, the carbon was prewetted under a vacuum to remove air from the carbon pores.

If the bulk densities or void fractions—or both—of the RSSCT and pilot columns are significantly different, the volume of water treated per mass of GAC for both the RSSCT and pilot column should be used to represent performance rather than elapsed time.

In addition, the impact of bulk density and void fraction differences between the pilot columns and the RSSCTs would be insignificant as long as the mass of carbon in the RSSCT is calculated from this equation:

$$M_{SC} = EBCT_{LC} \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{2-X} Q_{SC}\rho_{b,LC} \qquad (8)$$

in which M_{SC} and Q_{SC} are the mass of carbon and the flow rate, respectively, used in the RSSCT, and $\rho_{b,LC}$ is the bulk density of the full-scale column.

All chemicals used in this study were reagent grade or better.* Water for the low-DOC column influent and preparation of other solutions was distilled and deionized, followed by purification† and treatment with a large GAC column.

The volatile organic compounds (chloroform, dibromochloromethane, 1,2-dibromoethane, bromoform, trichloroethene, and tetrachloroethene) were analyzed using direct aqueous injection into a gas chromatograph (GC)‡ that was equipped with an electron capture detector. An 8-ft × 2-mm packed column§ was used to separate the compounds. Forty millilitres per minute of argon/methane (95:5 ratio) was used for a carrier gas. The initial oven temperature

*1,2-Dibromoethane, bromoform, dibromochloromethane, chloroform, trichloroethene and tetrachloroethene were obtained from Aldrich Chemical Co., Milwaukee, Wis. The activated carbon was Filtrasorb-400, Calgon Corp., Pittsburgh, Pa.

†Milli-Q, Millipore Corp., Bedford, Mass.

‡Model 5840, Hewlett-Packard, Avondale, Pa.

§3% SP-1500 on 80/120 mesh on Carbopack B, Supelco, Bellefonte, Pa.

of 120°C was maintained for 17 min; then the temperature was increased to 160°C in 1.6 min and held for 12 min. The injection port and detector temperatures were maintained at 210 and 350°C, respectively.

The nonpurgeable dissolved organic carbon (NPDOC) samples were analyzed using UV-light-promoted persulfate oxidation. The analysis was performed using a TOC analyzer* that had an autosampler with direct injection mode.

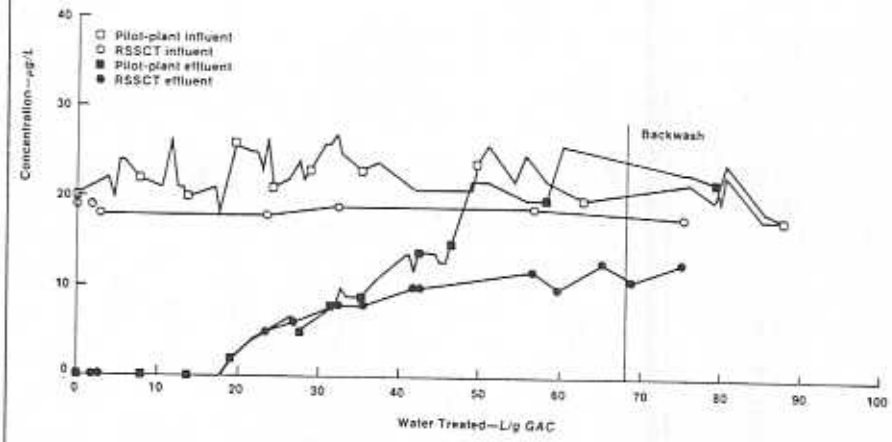


Figure 6. Comparison of CD-RSSCT[9] and pilot-column breakthrough data for 1,2-dichloropropane in a filtered groundwater (*pilot plant: loading rate—8.75 m/h, bulk density—440 kg/m³, EBCT—4.9 min; RSSCT: loading rate—65.87 m/h, bulk density—506.7 kg/m³, EBCT—0.086 min; pilot particle size—0.161 cm; RSSCT particle size—0.0212 cm*)

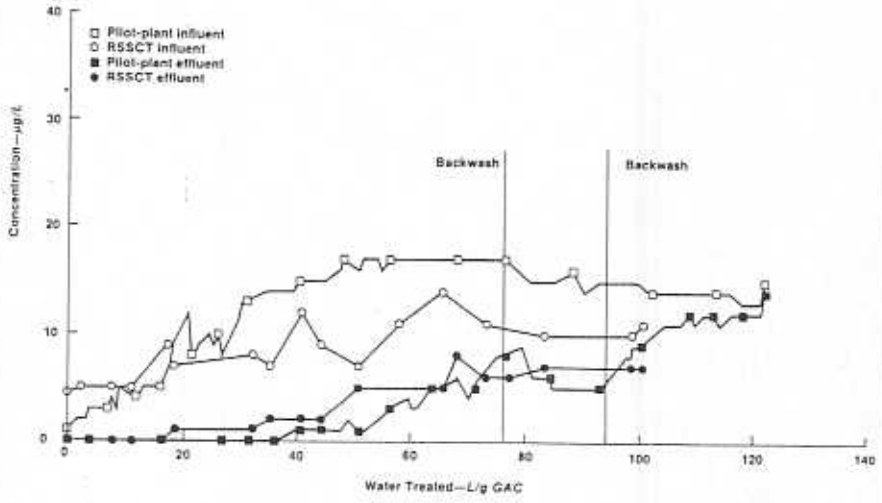


Figure 7. Comparison of CD-RSSCT and pilot-plant influent and effluent concentration profiles for aldicarb sulfoxide in Suffolk County, N.Y., groundwater (*pilot plant: loading rate—8.75 m/h, bulk density—440 kg/m³, EBCT—4.9 min; RSSCT: loading rate—65.87 m/h, bulk density—506.7 kg/m³, EBCT—0.086 min; the RSSCT was designed to simulate a pilot column with an EBCT of about 5 min;[9] pilot particle size—0.161 cm; RSSCT particle size—0.0212 cm*)

TABLE 3

*Successful attempts in using RSSCTs to predict pilot-column data compared with the number of studies conducted (indicated in parentheses)**

RSSCT Design	SOC Alone	SOC in the Presence of DOC		DOC Alone
		High SOC Concentration (>1,000 µg/L)	Low SOC Concentration (<300 µg/L)	
CD	3(4)	3(3)	6(10)	0(5)
PD		0(2)	1(1)	11(11)

*The second, third, and fourth columns are predictions of SOC removals, and the last column is DOC removal.

The methods used in the review of other studies[4,5,9-16] are described in the cited articles.

Results

Impact of biodegradation on RSSCT performance. In the development of the scaling equations, biodegradation was not considered and was found not to play an important role in the removal of SOCs or DOC in the studies that are reviewed here. However, if it is found to be important, it may increase SOC or DOC removal in the full-scale process. Because the run times for the RSSCTs are often too short to allow biodegradation to occur, the volume of treated water predicted from the RSSCT may be less than would be obtained from the full-scale process in cases in which biodegradation occurs. Thus, if biodegradation is important, then RSSCTs would provide conservative estimates of GAC performance.

Application of RSSCTs to predict the removal of SOCs. Table 1 summarizes 22 studies in which RSSCT effluent data were compared with results from pilot columns. These studies involved the adsorption of 12 different SOCs, including weakly adsorbing trihalomethanes and strongly adsorbing pesticides. The background water matrixes included a water that had been distilled, deionized, and GAC-filtered[4] (and this study), four groundwaters,[5,9,11,13,16] a lake water (this study), and a river water.[10] Three different scenarios were represented: (1) a low concentration of background organic matter and a relatively high concentration of the SOC—>1.0 mg/L[4] (and this study), (2) adsorbable background organic matter and a relatively high concentration of the SOC (this study), and (3) adsorbable background organic matter and a relatively low concentration of the SOC—<0.38 mg/L.[5,9-11,16] This study and two other studies[5,10] investigated both the proportional diffusivity (PD) design and constant diffusivity (CD) design, whereas the other studies used the CD design only.

Scenario 1. The two effluent profiles that are farthest to the right in Figures 1-3 represent scenario 1. These profiles are designated organic free water (OFW) in the figures, and the profiles in Figures 1-3 that are farthest to the right are the RSSCT data. These data were obtained by spiking the six compounds that are listed in Table 1 as studies 2 and 3 into distilled, deionized, and GAC-filtered water that had a DOC concentration of 0.2 mg/L. The CD RSSCT design using Eqs 1 and 2 yields good comparisons between the results of the RSSCT and pilot column with OFW for all six compounds and the two EBCTs that were tested. However, more capacity is ob-

*Model DC-180, Dohrmann, Rosemount, Calif.

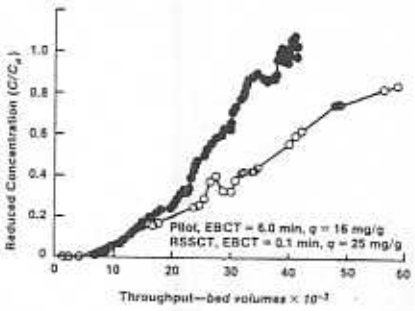
served in the RSSCT than in the pilot-plant test; this may be due to the pre-adsorption of the DOC that occurs in column tests.[17] These results confirm the earlier successful RSSCT results in Table 1, study 1, which had a very short EBCT. Studies 1-3 also illustrate the ability of the RSSCTs to predict the desorption of compounds caused by competitive adsorption and the resulting overshoot concentration for which the effluent concentration exceeds the influent concentration. In scenario 1, the high SOC concentration and the lack of transport hindrance by the background DOC create a situation in which external mass transfer is important and the CD design yields a similar amount of spreading in the breakthrough curve as in that of the pilot plant.

Additional studies were conducted for scenario 1. These studies used smaller GAC particle sizes in the RSSCTs and examined whether the RSSCTs could be conducted in a shorter time. These CD RSSCT designs, which utilized 100 × 140-mesh GAC, are reported in Table 1 as Studies 4 and 5. The resulting RSSCT effluent profiles (not presented here) appeared much earlier than in the pilot data. Rate studies demonstrated that the intraparticle diffusivity for the 100 × 140-mesh GAC was much smaller than that for the 12 × 40-mesh GAC.[18] Unlike the 60 × 80-mesh GAC, the external mass transfer resistance was not as important for the 100 × 140-mesh GAC, and this could have caused the earlier breakthrough for the RSSCT. Another problem encountered for the 100 × 140-mesh GAC is a very high head loss, which increased with time and caused early termination of the run. In addition, this high head loss may have caused channeling. Accordingly, RSSCTs with sizes smaller than 60 × 80 mesh are not recommended unless these problems are resolved.

Although the results in Figures 1-3 are very encouraging for scenario 1, it is important to recognize that good comparisons cannot be expected using the CD design when the intraparticle mass transfer rate is the controlling parameter. Figure 4 compares RSSCT effluent profiles with pilot data for a high concentration of methylene blue and a CD design that is designated as study 21 in Table 1. In this case, the larger size of methylene blue causes the intraparticle mass transfer rate to be controlling, and the intraparticle diffusion coefficient decreases dramatically with particle size. These facts explain why the RSSCT effluent profile appears before that of the pilot columns.

Scenario 2. The two data sets in Figures 1-3 that appear to the left of the low-DOC results represent scenario 2, and the first profile in each figure is the pilot-plant data. These data are reported as studies 6 and 7 in Table 1. The effluent data are reported in Figures 1-3 as natural organic matter (NOM) because the DOC background was of natural origin. As can be seen, a significantly earlier breakthrough occurred in the presence of lake water DOC than in the presence of low-DOC water for both the RSSCTs and the pilot plant. However, the CD design of the RSSCT predicts the pilot performance reasonably well for both scenarios 1 and 2.

The results of the PD-designed RSSCTs are designated as studies 8 and 9 in Table 1. The PD results, which are not plotted, showed that the RSSCTs had a much sharper breakthrough profile than the pilot columns. Using mass



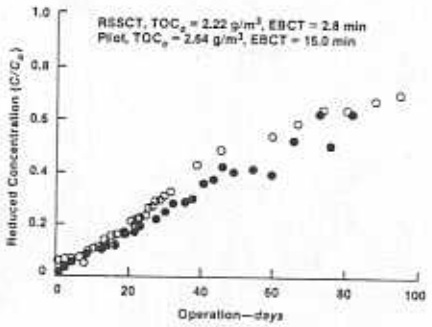
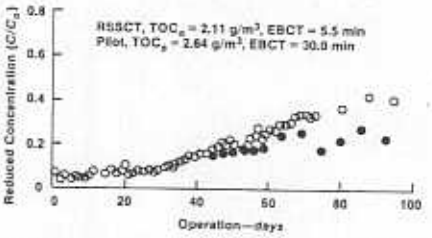


Figure 8. Comparison of CD-RSSCT[10] and pilot-column breakthrough data for trichloroethene in flocculated and filtered Rhine River water (*carbon—F-100; C_0—0.31 g/m³; DOC_0—2.25 g/m³; pilot particle size—0.18 cm; RSSCT particle size—0.022 cm*)



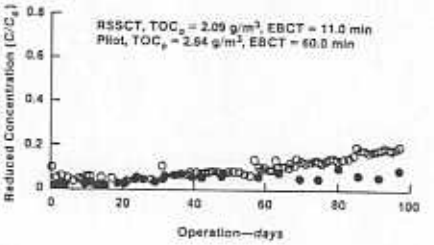


Figure 9. Comparison of PD-RSSCT[14] and pilot-column breakthrough data for TOC in flocculated and filtered Colorado River water (*carbon—F-400; pilot particle size—0.1026 cm; RSSCT particle size—0.0212 cm*)

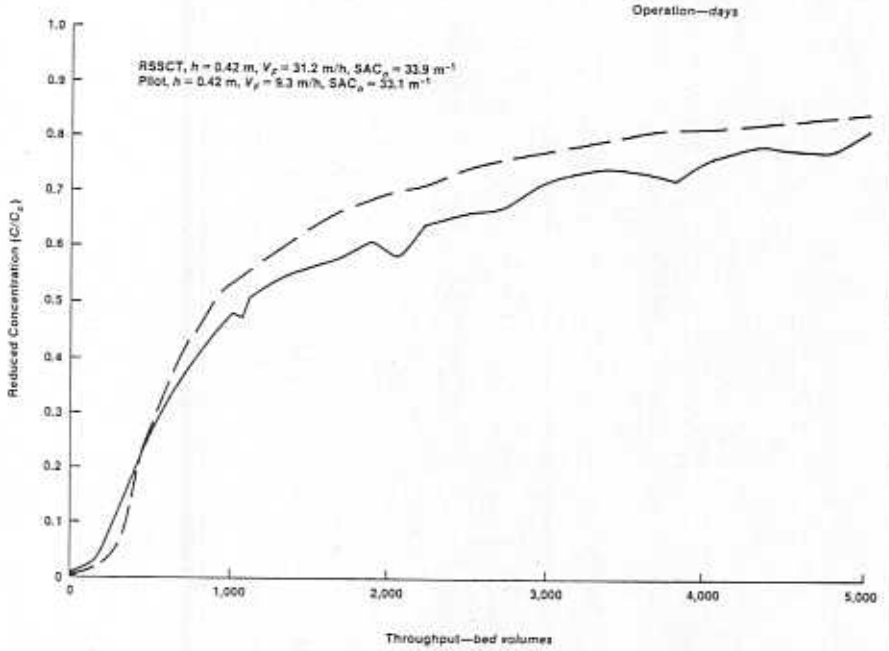


Figure 10. Comparison of PD-RSSCT[14] and pilot-column breakthrough data for UV absorbance (spectral absorption coefficient [SAC]) of humic substances spiked into GAC-treated tap water (groundwater) (*pilot particle size—0.085 cm; RSSCT particle size—0.026 cm*)

transfer models, Arora[19] showed that the external mass transfer resistance was important for studies 6–9. As discussed, the PD design reduces the amount of spreading in the breakthrough curve caused by external mass transfer, yielding sharper breakthrough profiles.

In an effort to examine the influence of the particle size distribution on RSSCT performance, the results from two additional RSSCTs were compared with the data from study 7. (Once again these comparisons are for scenario 2.) In Figure 5, CD-1 and the pilot data are from study 7. Some of these data were plotted in Figure 3. Test CD-2 represents the RSSCT that was conducted as a control to be identical to CD-1, and CD-mix is the RSSCT that had a particle size distribution. The CD-mix used GAC that had the same uniformity coefficient as that of the pilot plant, and this mixture of GAC was made from 10 percent of 45 × 50-mesh GAC, 30 percent of 60 × 70-mesh GAC, and 60 percent of 100 × 130-mesh GAC. The CD-2 and CD-mix tests are reported in Table 1 as study 22. For CD-2 and CD-mix, the same six compounds were spiked into the same lake water as in the pilot study and RSSCT CD-1. However, the DOC concentration was higher for the pilot study and CD-1 RSSCT. Figure 5 demonstrates that the results from the mixed-size RSSCT are identical to those for the 60 × 80-mesh RSSCT, CD-2, which was conducted at the same time. In addition, the higher DOC background concentration for CD-2 had a later breakthrough than for CD-1. Thus, the particle size distribution has no effect on RSSCT results. However, the DOC background concentration at the time the RSSCT is conducted has an impact on the results.

Scenario 3. Figures 6–8 represent a case of scenario 3.[9,10] In Figure 6, the RSSCT that utilizes a CD design predicts the pilot-column behavior for more than half of the breakthrough but has more adsorption capacity than the pilot column. This capacity difference, which is also evident in the data in Figures 1–3, represents a drawback of the RSSCT method. This problem is due to the difference in the adsorption and mass transfer kinetics of the SOC and the components in the background organic matter that foul the surface of the carbon.[17] If the SOC and the fouling component of DOC are not modeled by the same scaling equations, then the RSSCTs cannot accurately predict the pilot-column results.[17] The impact of this problem is also evident in the study by Speth and Miltner[11] in which a 20–40 percent difference in adsorption capacity was observed and reported in Table 1, study 19. In Figure 8, Summers et al[10] observed a 50 percent difference in capacity for the SOC in the presence of a river water. Summers et al[10] also designed a PD RSSCT, but the capacity differences between the RSSCT and pilot-column GAC still dominated the comparison. In study 13,[5] a PD-designed RSSCT resulted in a better comparison for low SOC concentrations in the presence of a groundwater DOC in terms of both adsorption capacity and kinetics.

Based on these case studies, the RSSCT approach appears to be very useful, but the appropriate design for the RSSCT cannot be decided without at least one comparison with pilot data. For waters in which the background organic matter causes a difference in the RSSCT and pilot-column GAC adsorption capacities, some preexposure to the DOC may be required to obtain good results.[16] However, experience for RSSCTs that use 60 × 80-mesh GAC and a CD design shows that the capacity and bed life predicted by RSSCTs are typically only 20–40 percent larger than those observed in pilot tests; this may be precise enough for preliminary design work.

Application of RSSCTs to predict DOC removal. Table 2 summarizes the results of 11 comparisons of RSSCT and pilot columns. These studies involved the adsorption of background organic matter as measured by total or dissolved organic carbon or UV absorbance. In the study by Wallace et al,[15] five different raw-water sources were used: Colorado River (CRW), California State Project (SPW), Ohio River, Mississippi River, and Delaware River. The EBCT of the pilot columns was 15 min for all sites except the Mississippi River and Colorado River. For CRW, a CD design yielded poor results, and RSSCT profiles appeared much earlier than those of the pilot columns. Vaitheeswaran et al[20] determined that the intraparticle diffusivity was proportional to particle size for CRW and SPW; consequently, PD designs were compared with pilot data for the other studies. Figure 9 reports the results for CRW; the PD RSSCT design yielded reasonable predictions of pilot performance for 15 min of EBCT. Breakthrough time in Figure 9 is expressed as equivalent operation time in the pilot column, and, as shown in Eq 6, this implies that the RSSCT (using a 60 × 80-mesh GAC) can be conducted in 20 percent of the time of the pilot test. Wallace et al[15] also examined other EBCTs for CRW, and, as shown in Figure 9, they found that for the 30- and 60-min EBCTs, the breakthrough of the RSSCTs appeared slightly after that of the pilot column. The PD design ($X = 1$, Eq 5) yielded good comparisons between the results of the RSSCT and the pilot columns for the other sites that are reported in Table 2.

Summers et al[14] investigated both the PD- and CD-designed RSSCTs for a series of four particle sizes. In their study, humic substances that had been extracted from a groundwater were added to tap water that had been previously treated by GAC to remove all adsorbable compounds. In addition to characterization by DOC, UV absorbance at 254 nm was measured. As was observed in the study by Wallace et al,[15] the results from the CD-designed RSSCTs showed an earlier breakthrough, which increased with decreasing particle size. The results from the PD-designed RSSCTs predicted the breakthrough from the pilot column, and the use of the UV absorbance spectral absorption coefficient to characterize the adsorption of these humic substances also proved successful, as shown in Figure 10.

In all cases investigated by Wallace et al[15] and Summers et al,[14] good comparisons between RSSCTs and pilot columns were obtained using a PD design. Therefore, if biodegradation of the DOC occurred, it did not appear to affect the RSSCT predictions. In the study by Summers et al,[14] the RSSCT even predicted the long-term DOC removal in pilot columns that were operated for more than a year.

In studies 6–9 in Table 1, in which the six compounds were spiked into lake water, the NPDOC effluent profiles for RSSCTs and pilot plants were compared, but neither the PD- nor the CD-designed RSSCTs were able to adequately predict the pilot-column DOC breakthrough. This may have been a result of a fourfold increase in the influent concentration to the pilot column during the middle of the run, or it may have been due to the presence of six halogenated organic compounds, each with a concentration in the range 0.9–1.8 mg/L, that dominated the organic carbon fraction.

Summary and conclusions

The use of small-scale columns (RSSCTs) has the potential to be a major breakthrough in predicting the behavior of full-scale GAC columns. This method has several advantages over the other approaches used in the design of GAC columns. It assesses both the adsorption capacity and kinetics, it has low capital and operational costs, and it does not require the use of numerical models.

Several problems still exist with the a priori design of the small-scale columns for the removal of SOCs because of the presence of interfering background organic matter and the particle size dependence of the intraparticle diffusivity. Experience to date indicates a CD-designed RSSCT is appropriate when external mass transfer is an important mass transfer resistance or when the intraparticle diffusivity is found not to be a function of particle size. Proportional diffusivity design is appropriate when internal diffusion controls the adsorption rate and the intraparticle diffusivity is a linear function of particle size. The data

summarized in Table 3 suggest that satisfactory RSSCT results can be obtained for one- to three-carbon alkanes and alkenes and simple substituted ring structures using a CD design and 60 × 80-mesh-size GAC. Particle sizes smaller than 60 × 80 mesh using a CD design resulted in high head loss and poor results. Background organic matter has been shown to decrease, up to 50 percent, the adsorption capacity of the pilot column compared with the RSSCTs, which cannot be predicted a priori. Accordingly, the RSSCTs can only be used to obtain preliminary design information. For more precise design information, a pilot-column run is needed to calibrate the RSSCT, after which the small-scale columns can be used to (1) evaluate design parameters, such as EBCT and parallel and series operation; (2) assess pretreatment options, such as ozonation; and (3) assess influent variations, such as concentration or background organic matter, as was demonstrated as part of this study. The small-scale columns can be used directly to selectively screen different GACs prior to pilot testing, which will reduce the costs of the pilot system.

Although the testing was limited to six raw-water sources, the success of the small columns in predicting the breakthrough of DOC in the pilot columns (summarized in Table 3) indicates that the PD design approach can be used in the design of full-scale systems as long as removal of DOC by biological growth is not important.

For a CD design, an RSSCT using 60× 80-mesh GAC and an 11-mm-ID column can be conducted in 4.2 percent of the time that is required for a pilot study that uses 12 × 40-mesh GAC and in 1.7 percent of the time needed for a pilot column that uses 8 × 30-mesh GAC. Constant diffusivity RSSCTs require 231 and 95.4 L of water to simulate 100 days of pilot-plant performance with a 5 m/h hydraulic loading and 12×40- and 8 × 30-mesh GACs, respectively. In contrast, a 51-mm-ID pilot plant with a 5-m/h hydraulic loading requires 25,000 L of water for 100 days of operation. For an equivalent PD-design RSSCT, the run time would be 20.7 percent of the time that is required for a pilot plant that uses 12×40-mesh GAC and 13 percent of the time for a pilot column that uses 8 × 30-mesh GAC. The PD RSSCTs would require 322 and 204 L of water to simulate pilot results for 12×40- and 8×30-mesh GACs, respectively.

Acknowledgment

The National Science Foundation (Award CES-8603615) Division of Fundamental Research for Emerging and Critical Engineering Systems provided support for the pilot testing on the removal of SOCs, and the AWWA Research Foundation (Contract 230-86) provided the support for the RSSCTs. Some cost-sharing support was provided by the Department of Civil Engineering and the Environmental Engineering Center for Water and Waste Management at Michigan Technological University. The RSSCT and pilot data on removal of SOCs from groundwater at Suffolk County, N.Y., were provided by Joe Baier at Suffolk County Department of Health Services, Hauppauge. The RSSCT and pilot data on removal of DOC were provided by I. Elaine Wallace, E. Marco Aieta, and Carol Tate at James M. Montgomery, Consulting Engineers Inc., Pasadena, Calif., and Michael J. McGuire at the Metropolitan Water District of Southern California, Los Angeles.

References

1. FRICK, B.R. Theoretische Betrachtungen zu den Problemen des Scale-up von Aktiukohlefest belt Adsorbern. Heft 20, Engler-Bunte-Institut, Univ. of Karlsruhe, FRG (1982).
2. ROSENE, M.R. ET AL. High Pressure Technique for Rapid Screening of Activated Carbons for Use in Potable Water. *Activated Carbon Adsorption, Volume I* (I.R. Suffet and M.J. McGuire, editors). ACS, Philadelphia, Pa. (1983).
3. BILELLO, L.J. & BEAUDET, B.A. Evaluation of Activated Carbon by the Dynamic Minicolumn Adsorption Technique. *Treatment of Water by Activated Carbon* (I.R. Suffett and M.J. McGuire, editors). ACS, Philadelphia, Pa. (1983).
4. CRITTENDEN, J.C.; BERRIGAN, J.K.; & HAND, D. W. Design of Rapid Small-Scale Adsorption Tests for a Constant Diffusivity. *Jour. WPCF*, 58:4:312 (1986).
5. CRITTENDEN, J.C. ET AL. Design of Rapid Fixed-Bed Adsorption Tests for Non-Constant Diffusivities. *Jour. Envir. Engrg.*, 113:2:243 (1987).
6. WEBER, W.J. & WANG, C. A Microscale System for Estimation of Model Parameters for Fixed-Bed Adsorbers. *Envir. Sci. & Technol.* 21:1096 (1987).
7. BERRIGAN, J.K. Scale Up of Rapid Small Scale Adsorption Test to Field Scale Adsorber: Theoretical and Experimental Basis. Master's thesis, Michigan Technol. Univ., Houghton (1985).
8. MARTIN, H. Low Peclet Number Particle-to-Fluid Heat and Mass Transfer in Packed Bed. *Chem. Engrg. Sci.*, 33:913 (1978).
9. HINELINE, D.W.; CRITTENDEN, J.C.; & HAND, D.W. Rapid Small-Scale Column Tests to Predict Full-Scale Adsorber Capacity and Performance. Proc. 1987 AWWA Ann. Conf., Kansas City, Mo.
10. SUMMERS, R.S. ET AL. The Influence of Background Organic Matter on GAC Adsorption. *Jour. AWWA*, 81:5:66 (May 1989).
11. SPETH, T.F. & MILTNER, R.S. Effect of Preloading on the Scale-up of GAC Microcolumns. *Jour. AWWA*, 81:4:141 (Apr. 1989).
12. TRYNOSKI, J.M. The Role of the Particle Size Distribution in Rapid Small-Scale Column Tests. Master's thesis, Michigan Technol. Univ., Houghton (1989).
13. NIEHAUS, S.L. ET AL. RSSCT and Pilot-Scale Tests on Methylene Blue. Unpubl. rept. submitted to the Dept. of Civil and Envir. Engrg., Michigan Technol. Univ., Houghton (1989).
14. SUMMERS, R.S. ET AL. Adsorption of Dissolved Organic Carbon by Activated Carbon: Scale-up, Modeling, and Desorption. Proc. 1989 AWWA Ann. Conf., Los Angeles, Calif.
15. WALLACE, I.E. ET AL. The Application of the Rapid Small-Scale Column Test to Model Organic Removal by Granular Activated Carbon. Proc. 1988 AWWA Ann. Conf., Orlando, Fla.
16. SPETH, T. Evaluating Capacities of Granular Activated Carbon Preloaded With a Natural Water. Proc. 1989 AWWA Ann. Conf., Los Angeles, Calif.
17. SONTHEIMER, H.; CRITTENDEN, J.C.; & SUMMERS, S. Activated Carbon for Water Treatment. DVGW-Forschungsstelle am Engler-Bunte-Institut der Universitat Karlsruhe, Karlsruhe, FRG. Distributed in the US by AWWARF, Denver, Colo. (2nd ed. 1988).
18. CRITTENDEN, J.C. ET AL. Prediction of GAC Performance Using Rapid Small-Scale Column Tests. AWWARF Rept. AWWARF, Denver, Colo. (1989).
19. ARORA, H. Modeling of Fixed-Bed Adsorbers for Multicomponent Mixture Consisting of Known and Unknown Components. Doctoral dissertation, Michigan Technol. Univ., Houghton (1988).
20. VAITHEESWARAN, K. ET AL. Prediction of the Removal of Dissolved Organic Carbon by Fixed-Bed Adsorbers. Proc. 1988 AWWA Ann. Conf., Orlando, Fla.

About the authors: *John C. Crittenden is a presidential professor of civil and environmental engineering at Michigan Technological University, 1400 Townsend Dr., Houghton, MI 49931. A graduate of the University of Michigan, Ann Arbor (BSE, MSE, and Ph.D.), Crittenden has received awards from AWWA for academic achievement and for best papers published in* JOURNAL AWWA *and an award from ASCE for best paper in the* Journal of Environmental Engineering. *Parimi Sanjay Reddy is an engineer with Environmental Science & Engineering, 744 Thimbleshoals Blvd., Newport News, VA 23606. Harish Arora is a project engineer with Malcolm Pirnie, Inc., 100 Eisenhower Dr., Paramus, NJ 07653. John Trynoski is a sanitary process environmental engineer at Donahue & Associates, 4738 N. 40th St., Sheboygan, WI 53083. David W. Hand is a senior research engineer and David L. Perram is an assistant research scientist in the Environmental Engineering Center at Michigan Technological University. R. Scott Summers is assistant professor of civil and environmental engineering, University of Cincinnati, 741 Baldwin (ML71), Cincinnati, OH 45221-0071.*

Appendix 19

SOP –Carbon Column (GAC)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Carbon Column (GAC)

I. Scope and Application

This standard operating procedure (SOP) describes the procedure for performing Carbon Column (GAC) Tests as part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

Hudson River dredged material may be transported to land-based processing facilities, where aqueous streams would need treatment prior to discharge. Granular activated carbon (GAC) would likely be used for final polishing of treated water.

The primary objective of the Carbon Column (GAC) tests is to demonstrate the PCB removals and effluent quality that can be expected following GAC treatment at typical design loading conditions of 20 to 40 minutes empty bed contact times (EBCT). GAC feed streams will be generated from treatment of several dredged material slurry simulations to represent the range of PCB concentrations that may be expected during dredging operations.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (BBL, 2003);
- Two Lexan or glass columns, 4-inches diameter x 6-feet high, piped in series;
- Gravel/coarse sand underdrain;
- Activated carbon, 36-inch bed depth.
- Feed pump: 0.1 to 1 gallons per minute (gpm) positive displacement;
- Sample containers; and
- Laboratory notebook.

III. Health and Safety Considerations

Refer to the Revised HASP (BBL, 2003).

IV. Carbon Column (GAC) Test Procedure

Procedures for the GAC column tests are described below:

1. The GAC columns will be backwashed to a 1.5:1 expansion volume before each hydraulically dredged material simulation feed at the three GAC loading rates.

2. Each of the MMF filtered water samples will be fed at empty-bed contact times (EBCTs) of 60, 20, and 12 minutes, corresponding to upstream MMF loadings of 2, 6, and 10 gpm per square foot (sq ft). For a 4-inch-diameter column, these loadings are attained at flow rates of 0.17, 0.52, and 0.87 gpm. Check feed rate by volumetric measurement of effluent with timer. The second carbon column in series will represent EBCT loadings of 120, 40, and 24 minutes, respectively.

3. Samples of influent and effluent will be obtained after filtration of 10 bed volumes (100 L or 26 gallons) at each hydraulic loading rate.

4. Aliquots of feed and filtered samples will be analyzed for parameters listed in Table 2 of the TS Work Plan.

Note: The principal purpose of these tests is to confirm attainable removal rates for various constituents from a variety of simulated and treated dredged material slurries. The run lengths are abbreviated and are not expected to terminate because of treated constituent breakthrough. Pressures and headlosses are not monitored. Adsorption capacity and bed life will be estimated using Rapid Small-scale Column Tests (RSSCTs), described in a separate SOP.

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 20

SOP – Storage/Transport Study

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Storage/Transport Study

I. Scope and Application

This standard operating procedure (SOP) describes the procedure for the storage/transport study for stabilized/solidified sediments. These tests are part of treatability studies described in the Hudson River PCBs Superfund Site Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003).

The purpose of stabilization/solidification is to prevent transport of contaminants from the solids matrix and to produce a material with physical properties compatible with landfill disposal. The purpose of this study is to simulate motion similar to that which might be imparted during transport of stabilized/solidified sediments to a landfill destination. The transport-simulated samples will then be examined and tested for free water.

II. Equipment List

The following materials, as required, will be available during this procedure:

- Health and safety equipment (as required in the *Revised Health and Safety Plan* [Revised HASP]) (Blasland, Bouck & Lee, Inc. [BBL], 2003);
- Lexan tubing: 3-in. inside diameter by 24 inches; and
- Laboratory shaker with variable control.

III. Health and Safety Considerations

Refer to Revised HASP (BBL, 2003).

IV. Procedure for Storage/Transport Study

Select control samples of M1 (mechanical dredged sediment simulation) sediment which have not received any stabilization/solidification treatment. Select stabilized/solidified sediment samples which have cured for a period of at least 3 days. Select samples of filter press cake from treatment of hydraulic-transport sediment slurry.

Prepare 24-inch sections of Lexan tubing by sealing one end. Place approximately 2 Kg of each sample into the Lexan tubing by filling to a depth of approximately 18 inches. Tap lightly, then mark and record the sediment depth in each tube. Seal the upper end of the tube to prevent desiccation.

Bundle the tubes and place them upright in the shaker. Secure the bundle to the shaker. Set the shaker to a rotation speed of 60 rpm. Continue slow shaking for a duration of 5 days.

After the simulated transit period, remove the tubes from the shaker. Allow the tubes to stand undisturbed for 2 to 4 hours. After that time observe the sediment surface of each tube. Mark and measure the sediment surface in each tube. Note and measure any stratification or liquid accumulation on the surface or the bottom. Submit samples for Paint Filter test (see separate SOP).

V. References

BBL. 2003. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Appendix 21

SOP – One-Dimensional Consolidation (ASTM D2435)

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Designation: D 2435 – 96

Standard Test Method for One-Dimensional Consolidation Properties of Soils[1]

This standard is issued under the fixed designation D 2435; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope *

1.1 This test method covers procedures for determining the magnitude and rate of consolidation of soil when it is restrained laterally and drained axially while subjected to incrementally applied controlled-stress loading. Two alternative procedures are provided as follows:

1.1.1 *Test Method A*—This test method is performed with constant load increment duration of 24 h, or multiples thereof. Time-deformation readings are required on a minimum of two load increments.

1.1.2 Test Method B—Time-deformation readings are required on all load increments. Successive load increments are applied after 100 % primary consolidation is reached, or at constant time increments as described in Test Method A.

NOTE 1—The determination of the rate and magnitude of consolidation of soil when it is subjected to controlled-strain loading is covered by Test Method D 4186.

1.2 This test method is most commonly performed on undisturbed samples of fine grained soils naturally sedimented in water, however, the basic test procedure is applicable, as well, to specimens of compacted soils and undisturbed samples of soils formed by other processes such as weathering or chemical alteration. Evaluation techniques specified in this test method are generally applicable to soils naturally sedimented in water. Tests performed on other soils such as compacted and residual (weathered or chemically altered) soils may require special evaluation techniques.

1.3 It shall be the responsibility of the agency requesting this test to specify the magnitude and sequence of each load increment, including the location of a rebound cycle, if required, and, for Test Method A, the load increments for which time-deformation readings are desired.

NOTE 2—Time-deformation readings are required to determine the time for completion of primary consolidation and for evaluating the coefficient of consolidation, c_v. Since c_v varies with stress level and load increment (loading or unloading), the load increments with timed readings must be selected with specific reference to the individual project. Alternatively, the requesting agency may specify Test Method B wherein the time-deformation readings are taken on all load increments.

1.4 The values stated in SI units are to be regarded as the standard. The values stated in inch-pound units are approximate and given for guidance only. Reporting of test results in units other than SI shall not be regarded as nonconformance with this test method.

1.4.1 In the engineering profession it is customary practice to use, interchangeably, units representing both mass and force, unless dynamic calculations ($F = Ma$) are involved. This implicitly combines two separate systems of units, that is, the absolute system and the gravimetric system. It is scientifically undesirable to combine two separate systems within a single standard. This test method has been written using SI units; however, inch-pound conversions are given in the gravimetric system, where the pound (lbf) represents a unit of force (weight). The use of balances or scales recording pounds of mass (lbm), or the recording of density in lb/ft^3 should not be regarded as nonconformance with this test method.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 422 Method for Particle-Size Analysis of Soils[2]

D 653 Terminology Relating to Soil, Rock, and Contained Fluids[2]

D 854 Test Method for Specific Gravity of Soils[2]

D 1587 Practice For Thin-Walled Tube Geotechnical Sampling of Soils[2]

D 2216 Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock[2]

D 2487 Classification of Soils for Engineering Purposes[2]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[2]

D 3550 Practice for Ring-Lined Barrel Sampling of Soils[2]

D 3740 Practice for Minimum Requirements for Agencies Engaged in the Testing or Inspection, or both, of Soil and Rock as Used in Engineering Design and Construction[2]

D 4186 Test Method for One-Dimensional Consolidation

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of subcommitteeD18.05 on Structural Properties of Soil.

Current edition approved June 10, 1996. Published August 1996. Originally published as D 2435 – 65T. Last previous edition D 2435 – 90.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

*A Summary of Changes section appears at the end of this standard.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States.

Properties of Soils Using Controlled-Strain Loading[2]
D4220 Practice for Preserving and Transporting Soil Samples[2]
D 4318 Test Method for Liquid Limit, Plastic Limit, and Plasticity Index of Soils[2]
D 4452 Methods for X-Ray Radiography of Soil Samples[2]
D 4546 Test Methods for One-Dimensional Swell or Settlement Potential of Cohesive Soils[2]

3. Terminology

3.1 *Definitions*—The definitions of terms used in this test method shall be in accordance with Terminology D 653.

4. Summary of Test Method

4.1 In this test method a soil specimen is restrained laterally and loaded axially with total stress increments. Each stress increment is maintained until excess pore water pressures are completely dissipated. During the consolidation process, measurements are made of change in the specimen height and these data are used to determine the relationship between the effective stress and void ratio or strain, and the rate at which consolidation can occur by evaluating the coefficient of consolidation.

5. Significance and Use

5.1 The data from the consolidation test are used to estimate the magnitude and rate of both differential and total settlement of a structure or earthfill. Estimates of this type are of key importance in the design of engineered structures and the evaluation of their performance.

5.2 The test results can be greatly affected by sample disturbance. Careful selection and preparation of test specimens is required to minimize disturbance.

NOTE 3—Notwithstanding the statement on precision and bias contained in this standard, the precision of this test method is dependent on the competence of the personnel performing the test and suitability of the equipment and facilities used. Agencies that meet the criteria of Practice D 3740 generally are considered capable of competent and objective testing. Users of this test method are cautioned that compliance with Practice D 3740 does not assure reliable testing. Reliable testing depends on many factors, and Practice D 3740 provides a means of evaluation some of these factors.

5.3 Consolidation test results are dependent upon the magnitude of the load increments. Traditionally, the load is doubled for each increment resulting in a load-increment ratio of 1. For undisturbed samples, this load procedure has provided data from which estimates of the preconsolidation pressure also referred to as the maximum past pressure, using established evaluation techniques, compare directly with field measurement. Other load schedules may be used to model particular field conditions or meet special requirements. For example, it may be desirable to inundate and load the specimen in accordance with the wetting or loading pattern expected in the field in order to best simulate the response. Smaller than standard load increment ratios may be desirable for soils that are highly sensitive or whose response is highly dependent on strain rate. The test method specified to estimate the preconsolidation pressure provides a simple technique to verify that one set of time readings are taken after the preconsolidation pressure. Several other evaluation techniques exist and may yield different estimates of the preconsolidation pressure. Therefore, the requesting agency may specify an alternate technique to estimate the preconsolidation pressure.

5.4 Consolidation test results are dependent upon the duration of each load increment. Traditionally, the load duration is the same for each increment and equal to 24 h. For some soils, the rate of consolidation is such that complete consolidation (dissipation of excess pore pressure) will require more than 24 h. The apparatus in general use does not have provisions for formal verification of pore pressure dissipation. It is necessary to use an interpretation technique which indirectly determines that consolidation is complete. This test method specifies two techniques, however the requesting agency may specify an alternative technique and still be in conformance with this test method.

5.5 The apparatus in general use for this test method does not have provisions for verification of saturation. Most undisturbed samples taken from below the water table will be saturated. However, the time rate of deformation is very sensitive to degree of saturation and caution must be exercised regarding estimates for duration of settlements when partially saturated conditions prevail. The extent to which partial saturation influences the test results may be a part of the test evaluation and may include application of theoretical models other than conventional consolidation theory. Alternatively, the test may be performed using an apparatus equipped to saturate the specimen.

5.6 This test method uses conventional consolidation theory based on Terzaghi's consolidation equation to compute the coefficient of consolidation, c_v. The analysis is based upon the following assumptions:

5.6.1 The soil is saturated and has homogeneous properties;

5.6.2 The flow of pore water is in the vertical direction;

5.6.3 The compressibility of soil particles and pore water is negligible compared to the compressibility of the soil skeleton;

5.6.4 The stress-strain relationship is linear over the load increment;

5.6.5 The ratio of soil permeability to soil compressibility is constant over the load increment; and

5.6.6 Darcy's law for flow through porous media applies.

6. Apparatus

6.1 *Load Device*—A suitable device for applying vertical loads or total stresses) to the specimen. The device should be capable of maintaining specified loads for long periods of time with an accuracy of ± 0.5 % of the applied load and should permit quick application of a given load increment without significant impact.

NOTE 4—Load application generally should be completed in a time corresponding to 0.01 t_{100} or less. For soils where primary consolidation is completed in 3 min, load application should be less than 2 s.

6.2 *Consolidometer*—A device to hold the specimen in a ring that is either fixed to the base or floating (supported by friction on periphery of specimen) with porous disks on each face of the specimen. The inside diameter of the ring shall be determined to a tolerance of 0.075 mm (0.003 in.). The consolidometer shall also provide a means of submerging the

specimen, for transmitting the concentric vertical load to the porous disks, and for measuring the change in height of specimen.

6.2.1 *Minimum Specimen Diameter*—The minimum specimen diameter shall be 50 mm (2.00 in.).

6.2.2 *Minimum Specimen Height*—The minimum initial specimen height shall be 12 mm (0.5 in.), but shall be not less than ten times the maximum particle diameter.

NOTE 5—If large particles are found in the specimen after testing, include in the report this visual observation or the results of a particle size analysis in accordance with Method D 422 (except the minimum sample size requirement shall be waived).

6.2.3 *Minimum Specimen Diameter-to-Height Ratio*—The minimum specimen diameter-to-height ratio shall be 2.5.

NOTE 6—The use of greater diameter-to-height ratios is recommended. To minimize the effects of friction between the sides of the specimen and ring, a diameter-to-height ratio greater than four is preferable.

6.2.4 *Specimen Ring Rigidity*—The rigidity of the ring shall be such that, under hydrostatic stress conditions in the specimen, the change in diameter of the ring will not exceed 0.03 % of the diameter under the greatest load applied.

6.2.5 *Specimen Ring Material*—The ring shall be made of a material that is noncorrosive in relation to the soil tested. The inner surface shall be highly polished or shall be coated with a low-friction material. Silicone grease or molybdenum disulfide is recommended; polytetrafluoroethylene is recommended for nonsandy soils.

6.3 *Porous Disks*—The porous disks shall be of silicon carbide, aluminum oxide, or similar noncorrosive material. The grade of the disks shall be fine enough to prevent intrusion of soil into the pores. If necessary, a filter paper (see Note 7) may be used to prevent intrusion of the soil into the disks; however, the permeability of the disks, and filter paper, if used, must be at least one order of magnitude higher than that of the specimen.

NOTE 7—Whatman No. 54 filter paper has been found to meet requirements for permeability and durability.

6.3.1 *Diameter*—The diameter of the top disk shall be 0.2 to 0.5 mm (0.01 to 0.02 in.) less than the inside diameter of the ring. If a floating ring is used, the bottom disk shall have the same diameter as the top disk.

NOTE 8—The use of tapered disks is recommended, with the larger diameter in contact with the soil.

6.3.2 *Thickness*—Thickness of the disks shall be sufficient to prevent breaking. The top disk shall be loaded through a corrosion-resistant plate of sufficient rigidity to prevent breakage of the disk.

6.3.3 *Maintenance*—The disks shall be clean and free from cracks, chips, and nonuniformities. New porous disks should be boiled for at least 10 minutes and left in the water to cool to ambient temperature before use. Immediately after each use, clean the porous disks with a nonabrasive brush and boil to remove clay particles that may reduce their permeability. It is recommended that porous disks be stored in a jar with deaired water between tests.

6.4 *Specimen Trimming Device*—A trimming turntable or a cylindrical cutting ring may be used for trimming the sample down to the inside diameter of the consolidometer ring with a minimum of disturbance. A cutter having the same inside diameter as the specimen ring shall attach to or be integral with the specimen ring. The cutter shall have a sharp edge, a highly polished surface and be coated with a low-friction material. Alternatively, a turntable or trimming lathe may be used. The cutting tool must be properly aligned to form a specimen of the same diameter as that of the ring.

6.5 *Deformation Indicator*—To measure change in specimen height, with a readability of 0.0025 mm (0.0001 in.).

6.6 *Miscellaneous Equipment*—Including timing device with 1 s readability, distilled or demineralized water, spatulas, knives, and wire saws, used in preparing the specimen.

6.7 *Balances*, in accordance with Method D 2216.

6.8 *Drying Oven*, in accordance with Method D 2216.

6.9 *Water Content Containers*, in accordance with Method D 2216.

6.10 Environment—Tests shall be performed in an environment where temperature fluctuations are less than ± 4°C (± 7°F) and there is no direct exposure to sunlight.

7. Sampling

7.1 Practices D 1587 and D 3550 cover procedures and apparatus that may be used to obtain undisturbed samples generally satisfactory for testing. Specimens may also be trimmed from large undisturbed block samples fabricated and sealed in the field. Finally, remolded specimens may be prepared from bulk samples to density and moisture conditions stipulated by the agency requesting the test.

7.2 Undisturbed samples destined for testing in accordance with this test method shall be preserved, handled, and transported in accordance with the practices for Group C and D samples in Practices D 4220. Bulk samples for remolded specimens should be handled and transported in accordance with the practice for Group B samples.

7.3 *Storage*—Storage of sealed samples should be such that no moisture is lost during storage, that is, no evidence of partial drying of the ends of the samples or shrinkage. Time of storage should be minimized, particularly when the soil or soil moisture is expected to react with the sample tubes.

7.4 The quality of consolidation test results diminishes greatly with sample disturbance. It should be recognized that no sampling procedure can ensure completely undisturbed samples. Therefore, careful examination of the sample is essential in selection of specimens for testing.

NOTE 9—Examination for sample disturbance, stones, or other inclusions, and selection of specimen location is greatly facilitated by x-ray radiography of the samples (see Methods D 4452).

8. Calibration

8.1 The measured vertical deformations must be corrected for apparatus flexibility whenever the calibration correction determined in 8.4 exceeds 5 % of the measured deformation and in all tests where filter paper disks are used.

8.2 Assemble the consolidometer with a copper or hard steel disk of approximately the same height as the test specimen and 1 mm (0.04 in.) smaller in diameter than the ring, in place of the sample. Moisten the porous disks. If filter papers are to be used (see 6.3), they should be moistened and sufficient time (a

minimum of 2 min.) allowed for the moisture to be squeezed from them during each increment of the calibration process.

8.3 Load and unload the consolidometer as in the test and measure the deformation for each load applied. When filter papers are used it is imperative that calibration be performed following the exact loading and unloading schedule to be used. This is due to the inelastic deformation characteristics of filter paper. Recalibration for tests without filter paper need be done only on an annual basis, or after replacement and reassembly of apparatus components.

8.4 At each load applied, plot or tabulate the corrections to be applied to the measured deformation of the test specimen. Note that the metal disk will deform also; however, the correction due to this deformation will be negligible for all but extremely stiff soils. If necessary, the compression of the metal disk can be computed and applied to the corrections.

9. Specimen Preparation

9.1 All possible precautions should be taken to minimize disturbance of the soil or changes in moisture and density during specimen preparation. Avoid vibration, distortion, and compression.

9.2 Prepare test specimens in an environment where soil moisture change during preparation is minimized.

NOTE 10—A high humidity environment is usually used for this purpose.

9.3 Trim the specimen and insert it into the consolidation ring. When specimens come from undisturbed soil collected using sample tubes, the inside diameter of the tube shall be at least 5 mm (0.25 in.) greater than the inside diameter of the consolidation ring, except as noted in 9.4 and 9.5. It is recommended that either a trimming turntable or cylindrical cutting ring be used to cut the soil to the proper diameter. When using a trimming turntable, make a complete perimeter cut, reducing the specimen diameter to the inside diameter of the consolidation ring. Carefully insert the specimen into the consolidation ring, by the width of the cut, with a minimum of force. Repeat until the specimen protrudes from the bottom of the ring. When using a cylindrical cutting ring, trim the soil to a gentle taper in front of the cutting edge. After the taper is formed, advance the cutter a small distance to form the final diameter. Repeat the process until the specimen protrudes from the ring.

9.4 Fibrous soils, such as peat, and those soils that are easily damaged by trimming, may be transferred directly from the sampling tube to the ring, provided that the ring has the same diameter as the sample tube.

9.5 Specimens obtained using a ring-lined sampler may be used without prior trimming, provided they comply with the requirements of Practice D 3550 and this test method.

9.6 Trim the specimen flush with the plane ends of the ring. The specimen may be recessed slightly below the top of the ring, to facilitate centering of the top stone, by partial extrusion and trimming of the bottom surface. For soft to medium soils, a wire saw should be used for trimming the top and bottom of the specimen to minimize smearing. A straightedge with a sharp cutting edge may be used for the final trim after the excess soil has first been removed with a wire saw. For stiff soils, a sharpened straightedge alone may be used for trimming the top and bottom. If a small particle is encountered in any surface being trimmed, it should be removed and the resulting void filled with soil from the trimmings.

NOTE 11—If, at any stage of the test, the specimen swells beyond its initial height, the requirement of lateral restraint of the soil dictates the use of a recessed specimen or the use of a specimen ring equipped with an extension collar of the same inner diameter as the specimen ring. At no time should the specimen extend beyond the specimen ring or extension collar.

9.7 Determine the initial wet mass of the specimen, M_{To}, in the consolidation ring by measuring the mass of the ring with specimen and subtracting the tare mass of the ring.

9.8 Determine the initial height, H_o, of the specimen to the nearest 0.025 mm (0.001 in.) by taking the average of at least four evenly spaced measurements over the top and bottom surfaces of the specimen using a dial comparator or other suitable measuring device.

9.9 Compute the initial volume, V_o, of the specimen to the nearest 0.25 cm^3 (0.015 $in.^3$) from the diameter of the ring and the initial specimen height.

9.10 Obtain two or three natural water content determinations of the soil in accordance with Method D 2216 from material trimmed adjacent to the test specimen if sufficient material is available.

9.11 When index properties are specified by the requesting agency, store the remaining trimmings taken from around the specimen and determined to be similar material in a sealed container for determination as described in Section 10.

10. Soil Index Property Determinations

10.1 The determination of index properties is an important adjunct to but not a requirement of the consolidation test. These determinations when specified by the requesting agency should be made on the most representative material possible. When testing uniform materials, all index tests may be performed on adjacent trimmings collected in 9.11. When samples are heterogeneous or trimmings are in short supply, index tests should be performed on material from the test specimen as obtained in 11.6, plus representative trimmings collected in 9.11.

10.2 *Specific Gravity*—The specific gravity shall be determined in accordance with Test Method D 854 on material from the sample as specified in 10.1. The specific gravity from another sample judged to be similar to that of the test specimen may be used for calculation in 12.2.5 whenever an accurate void ratio is not needed.

10.3 *Atterberg Limits*—The liquid limit, plastic limit and plasticity index shall be determined in accordance with Test Method D 4318 using material from the sample as specified in 10.1. Determination of the Atterberg limits are necessary for proper material classification but are not a requirement of this test method.

10.4 *Particle Size Distribution*—The particle size distribution shall be determined in accordance with Method D 422 (except the minimum sample size requirement shall be waived) on a portion of the test specimen as obtained in 11.6. A particle size analysis may be helpful when visual inspection indicates

that the specimen contains a substantial fraction of coarse grained material but is not a requirement of this test method.

11. Procedure

11.1 Preparation of the porous disks and other apparatus will depend on the specimen being tested. The consolidometer must be assembled in such a manner as to prevent a change in water content of the specimen. Dry porous disks and filters must be used with dry, highly expansive soils and may be used for all other soils. Damp disks may be used for partially saturated soils. Saturated disks may be used when the specimen is saturated and known to have a low affinity for water. Assemble the ring with specimen, porous disks, filter disks (when needed) and consolidometer. If the specimen will not be inundated shortly after application of the seating load (see 11.2), enclose the consolidometer in a loose fitting plastic or rubber membrane to prevent change in specimen volume due to evaporation.

NOTE 12—In order to meet the stated objectives of this test method, the specimen must not be allowed to swell in excess of its initial height prior to being loaded beyond its preconsolidation pressure. Detailed procedures for the determination of one-dimensional swell or settlement potential of cohesive soils is covered by Test Method D 4546.

11.2 Place the consolidometer in the loading device and apply a seating pressure of 5 kPa (100 lbf/ft^2). Immediately after application of the seating load, adjust the deformation indicator and record the initial zero reading, d_o. If necessary, add additional load to keep the specimen from swelling. Conversely, if it is anticipated that a load of 5 kPa (100 lbf/ft^2) will cause significant consolidation of the specimen, reduce the seating pressure to 2 or 3 kPa (about 50 lbf/ft^2) or less.

11.3 If the test is performed on an intact specimen that was either saturated under field conditions or obtained below the water table, inundate shortly after application of the seating load. As inundation and specimen wetting occur, increase the load as required to prevent swelling. Record the load required to prevent swelling and the resulting deformation reading. If specimen inundation is to be delayed to simulate specific conditions, then inundation must occur at a pressure that is sufficiently large to prevent swell. In such cases, apply the required load and inundate the specimen. Take time deformation readings during the inundation period as specified in 11.5. In such cases, note in the test report the pressure at inundation and the resulting changes in height.

11.4 The specimen is to be subjected to increments of constant total stress. The duration of each increment shall conform to guidelines specified in 11.5. The specific loading schedule will depend on the purpose of the test, but should conform to the following guidelines. If the slope and shape of a virgin compression curve or determination of the preconsolidation pressure is required, the final pressure shall be equal to or greater than four times the preconsolidation pressure. In the case of overconsolidated clays, a better evaluation of recompression parameters may be obtained by imposing an unload-reload cycle after the preconsolidation pressure has been defined. Details regarding location and extent of an unload-reload cycle is the option of the agency requesting the test (see 1.3), however, unloading shall always span at least two decrements of pressure.

11.4.1 The standard loading schedule shall consist of a load increment ratio (LIR) of one which is obtained by doubling the pressure on the soil to obtain values of approximately 12, 25, 50, 100, 200, etc. kPa (250, 500, 1000, 2000, 4000, etc. lbf/ft^2).

11.4.2 The standard rebound or unloading schedule should be selected by halving the pressure on the soil (that is, use the same increments of 11.4.1, but in reverse order). However, if desired, each successive load can be only one-fourth as large as the preceding load, that is, skip a decrement.

11.4.3 An alternative loading, unloading, or reloading schedule may be employed that reproduces the construction stress changes or obtains better definition of some part of the stress deformation (compression) curve, or aids in interpreting the field behavior of the soil.

NOTE 13—Small increments may be desirable on highly compressible specimens or when it is desirable to determine the preconsolidation pressure with more precision. It should be cautioned, however, that load increment ratios less than 0.7 and load increments very close to the preconsolidation pressure may preclude evaluation for the coefficient of consolidation, c_v, and the end-of-primary consolidation as discussed in Section 12.

11.5 Before each pressure increment is applied, record the height or change in height, d_f, of the specimen. Two alternative procedures are available that specify the time sequence of readings and the required minimum load duration. Longer durations are often required during specific load increments to define the slope of the characteristic straight line secondary compression portion of the deformation versus log of time graph. For such increments, sufficient readings should be taken near the end of the pressure increment to define this straight line portion. It is not necessary to increase the duration of other pressure increments during the test.

11.5.1 *Test Method A*—The standard load increment duration shall be 24 h. For at least two load increments, including at least one load increment after the preconsolidation pressure has been exceeded, record the height or change in height, d, at time intervals of approximately 0.1, 0.25, 0.5, 1, 2, 4, 8, 15 and 30 min, and 1, 2, 4, 8 and 24 h (or 0.09, 0.25, 0.49, 1, 4, 9 min etc. in using 12.3.2 to present time-deformation data), measured from the time of each incremental pressure application. Take sufficient readings near the end of the pressure increment period to verify that primary consolidation is completed. For some soils, a period of more than 24 h may be required to reach the end-of-primary consolidation (as determined in 12.3.1.1 or 12.3.2.3). In such cases, load increment durations greater than 24 h are required. The load increment duration for these tests is usually taken at some multiple of 24 h and should be the standard duration for all load increments of the test. The decision to use a time interval greater than 24 h is usually based on experience with particular types of soils. If, however, there is a question as to whether a 24 h period is adequate, a record of height or change in height with time should be made for the initial load increments in order to verify the adequacy of a 24 h period. Load increment durations other than 24 h shall be noted in the report. For pressure increments where time versus deformation data are not required, leave the load on the specimen for the same length of time as when time versus deformation readings are taken.

11.5.2 *Test Method B*—For each increment, record the height or change in height, d, at time intervals of approximately 0.1, 0.25, 0.5, 1, 2, 4, 8, 15, 30 min, and 1, 2, 4, 8 and 24 h (or 0.09, 0.25, 0.49, 1, 4, 9, min, etc. if using 12.3.2 to present time deformation data), measured from the time of each incremental pressure application. The standard load increment duration shall exceed the time required for completion of primary consolidation as determined by 12.3.1.1, 12.3.2.3 or a criterion set by the requesting agency. For each increment where it is impossible to verify the end of primary consolidation (for example, low LIR or rapid consolidation), the load increment duration shall be constant and exceed the time required for primary consolidation of an increment applied after the preconsolidation pressure and along the virgin compression curve. Where secondary compression must be evaluated, apply pressures for longer periods. The report shall contain the load increment duration for each increment.

NOTE 14—The suggested time intervals for recording height or change in height are for typical soils and load increments. It is often desirable to change the reading frequency to improve interpretation of the data. More rapid consolidation will require more frequent readings. For most soils, primary consolidation during the first load decrements will be complete in less time (typically one-tenth) than would be required for a load increment along the virgin compression curve, however, at very low stresses the rebound time can be longer.

11.6 To minimize swell during disassembly, rebound the specimen back to the seating load (5 kPa). Once height changes have ceased (usually overnight), dismantle quickly after releasing the final small load on the specimen. Remove the specimen and the ring from the consolidometer and wipe any free water from the ring and specimen. Determine the mass of the specimen in the ring and subtract the tare mass of the ring to obtain the final wet specimen mass, M_{T_f}. The most accurate determination of the specimen dry mass and water content is found by drying the entire specimen at the end of the test. If the soil sample is homogeneous and sufficient trimmings are available for the specified index testing (see 9.11), then determine the final water content, w_f, in accordance with Method D 2216 and dry mass of solids, M_d, using the entire specimen. If the soil is heterogeneous or more material is required for the specified index testing, then determine the final water content, w_{f_p}, in accordance with Method D 2216 using a small wedge shaped section of the specimen. The remaining undried material should be used for the specified index testing.

12. Calculation

12.1 Calculations as shown are based on the use of SI units. Other units are permissible, provided the appropriate conversion factors are used to maintain consistency of units throughout the calculations. See 1.4.1 for additional comments on the use of inch-pound units.

12.2 *Specimen Properties*:

12.2.1 Obtain the dry mass of the total specimen, M_d, by direct measurement or for the case where part of the specimen is used for index testing, calculate the dry mass as follows:

$$M_d = \frac{M_{T_f}}{1 + w_{f_p}}$$

where:

M_{Tf} = moist mass of total specimen after test, g or Mg, and

w_{f_p} = water content (decimal form) wedge of specimen taken after test.

12.2.2 Calculate the initial and final water content, in percent, as follows:

$$\text{initial water content: } w_o = \frac{M_{To} - M_d}{M_d} \times 100$$

$$\text{final water content: } w_f = \frac{M_{T_f} - M_d}{M_d} \times 100$$

where:

M_d = dry mass of specimen, g or Mg, and

M_{To} = moist mass of specimen before test, g or Mg.

12.2.3 Calculate the initial dry density of the specimen as follows:

$$\rho_d = \frac{M_d}{V_o}$$

where:

ρ_d = dry density of specimen, g/cm^3 or Mg/m^3, and

V_o = initial volume of specimen, cm^3 or m^3.

12.2.4 Calculate the dry unit weight of the specimen as follows:

$$\gamma_d = 9.8 \times \rho_d, \text{ in kN/m}^3$$

$$\gamma_d = 62.43 \times \rho_d, \text{ in lbf/ft}^3$$

12.2.5 Compute the volume of solids as follows:

$$V_s = \frac{M_d}{G\rho_w}$$

where:

G = specific gravity of the solids, and

ρ_w = density of water, 1.0 g/cm^3 or Mg/m^3

12.2.6 Since the cross-sectional area of the specimen is constant throughout the test, it is convenient for subsequent calculations to introduce the term "equivalent height of solids," defined as follows:

$$H_s = \frac{V_s}{A}$$

where:

A = specimen area, cm^2 or m^2.

12.2.7 Calculate void ratio before and after test as follows:

$$\text{void ratio before test: } e_o = \frac{H_o - H_s}{H_s}$$

$$\text{void ratio after test: } e_f = \frac{H_f - H_s}{H_s}$$

where:

H_o = initial specimen height, cm or m, and

H_f = final specimen height, cm or m.

12.2.8 Calculate the degree of saturation, in percent, before and after test as follows:

$$\text{initial degree of saturation: } S_o = \frac{M_{T_o} - M_d}{A\rho_w(H_o - H_s)} \times 100$$

final degree of saturation: $S_f = \frac{M_{T_f} - M_d}{A_{p_w}(H_f - H_s)} \times 100$

12.3 *Time-Deformation Properties*—From those increments of load where time-deformation readings are obtained, two alternative procedures (see 12.3.1 or 12.3.2) are provided to present the data, determine the end-of-primary consolidation and compute the rate of consolidation. Alternatively, the requesting agency may specify a method of its choice and still be in conformance with this test method. The deformation readings may be presented as measured deformation, deformation corrected for apparatus compressibility or converted to strain (see 12.4).

12.3.1 Referring to Fig. 2, plot the deformation readings, d, versus the log of time (normally in minutes) for each increment of load.

12.3.1.1 First draw a straight line through the points representing the final readings which exhibit a straight line trend and constant slope (**C**). Draw a second straight line tangent to the steepest part of the deformation-log time curve (**D**). The intersection represents the deformation, d_{100}, and time, t_{100}, corresponding to 100 % primary consolidation (**E**). Compression in excess of the above estimated 100 % primary consolidation is defined as secondary compression.

12.3.1.2 Find the deformation representing 0 % primary consolidation by selecting any two points that have a time ratio of 1 to 4. The deformation at the larger of the two times should be greater than ¼, but less than ½ of the total deformation for the load increment. The deformation corresponding to 0 % primary consolidation is equal to the deformation at the smaller time, less the difference in deformation for the two selected times.

12.3.1.3 The deformation, d_{50}, corresponding to 50 % primary consolidation is equal to the average of the deformations corresponding to the 0 and 100 % deformations. The time, t_{50}, required for 50 % consolidation may be found graphically from the deformation-log time curve by observing the time that corresponds to 50 % of the primary consolidation on the curve.

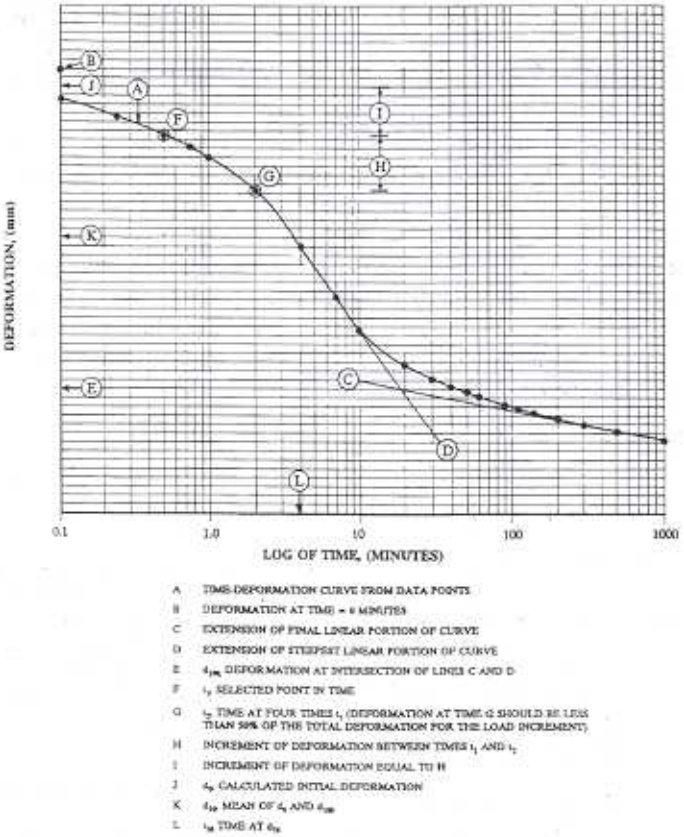


FIG. 2 Time-Deformation Curve From Log of Time Method

12.3.2 Referring to Fig. 3, plot the deformation readings, d, versus the square root of time (normally in minutes) for each increment of load.

12.3.2.1 First draw a straight line through the points representing the initial readings that exhibit a straight line trend. Extrapolate the line back to $t = 0$ and obtain the deformation ordinate representing 0 % primary consolidation.

12.3.2.2 Draw a second straight line through the 0 % ordinate so that the abscissa of this line is 1.15 times the

H_0=19.050 mm

H_s=8.538 mm

Void Ratio and Strain Information

Load Increment (kPa)	d_f corrected (mm)	$\Sigma\Delta H$ (mm)	ε $\Sigma\Delta H/H_0$ (%)	H $(H_0-\Delta H)$ (mm)	e $(H-H_s)/H_s$
initial	5.3300	0	0	19.0500	1.231
5	5.3012	0.0288	0.15	19.0212	1.228
10	5.2743	0.0557	0.29	18.9943	1.225
20	5.2167	0.1133	0.59	18.9367	1.218
40	5.1161	0.2139	1.12	18.8361	1.206
80	4.9433	0.3867	2.03	18.6633	1.186
160	4.4740	0.8560	4.49	18.1940	1.131
320	2.9804	2.3496	12.33	16.7004	0.956
640	1.8908	3.4392	18.05	15.6108	0.828
1280	0.9860	4.3440	22.80	14.7060	0.722
320	1.0747	4.2553	22.34	14.7947	0.733
80	1.4000	3.9300	20.63	15.1200	0.771
20	1.8169	3.5131	18.44	15.5369	0.820
5	2.2319	3.0981	16.26	15.9519	0.868

Coefficient of Consolidation, c_v

d_{50} corrected (mm)	$\Sigma\Delta H$ (mm)	ε_{50} (%)	H_{50} (mm)	e_{50}	t_{50} (sec)	c_v (mm^2/sec)
5.0604	0.2696	1.42	18.780	1.200	52	3.34×10^{-1}
4.7945	0.5355	2.81	18.515	1.169	144	1.17×10^{-1}
3.7861	1.5439	8.10	17.506	1.050	516	2.93×10^{-2}
2.4983	2.8317	14.86	16.218	0.900	282	4.59×10^{-2}
1.5077	3.8223	20.06	15.228	0.784	156	7.32×10^{-2}

FIG. 1 Consolidation Test Summary

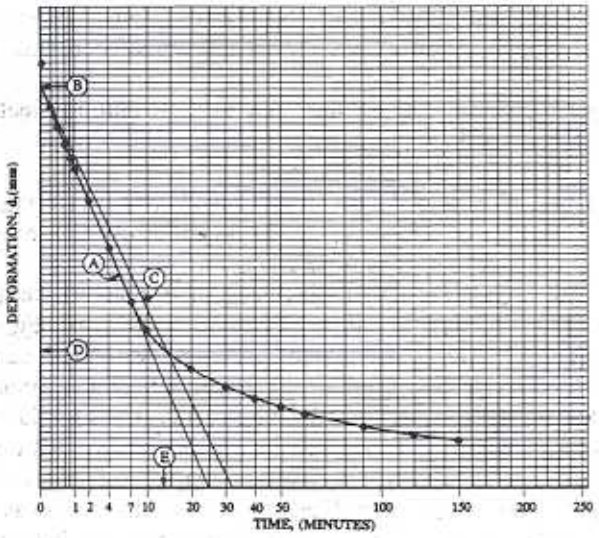


FIG. 3 Time-Deformation Curve From Square Root of Time Method

abscissa of the first straight line through the data. The intersection of this second line with the deformation-square root of time curve is the deformation, d_{90}, and time, t_{90}, corresponding to 90 % primary consolidation.

12.3.2.3 The deformation at 100 % consolidation is 1/9 more than the difference in deformation between 0 and 90 % consolidation. The time of primary consolidation, t_{100}, may be taken at the intersection of the deformation-square root of time curve and this deformation ordinate. The deformation, d_{50}, corresponding to 50 % consolidation is equal to the deformation at 5/9 of the difference between 0 and 90 % consolidation.

12.3.3 Compute the coefficient of consolidation for each increment of load using the following equation and values appropriate to the chosen method of interpretation:

$$c_v = \frac{TH^2_{D_{50}}}{t}$$

where:

T = a dimensionless time factor: for method 12.3.1 use 50 % consolidation with T $= T_{50} = 0.197$, for method 12.3.2 use 90 % consolidation with $T = T_{90} = 0.848$,

t = time corresponding to the particular degree of consolidation, s or min; for method 12.3.1 use $t = t_{50}$, for method 12.3.2 use $t = t_{90}$, and

$H_{D_{50}}$ = length of the drainage path at 50 % consolidation, cm or m for double-sided drainage $H_{D_{50}}$ is half the specimen height at the appropriate increment and for one-sided drainage $H_{D_{50}}$ is the full specimen height.

12.4 *Load-Deformation Properties:*

12.4.1 Tabulate the deformation or change in deformation, d_f, readings corresponding to the end of each increment and, if using Test Method B, corresponding to the end-of-primary consolidation, d_{100}.

12.4.2 Calculate the change in height, $\Delta H = d - d_o$, relative to the initial specimen height for each reading. If necessary, correct the deformation for the apparatus flexibility by subtracting the calibration value obtained in Section 9 from each reading.

12.4.3 Represent the deformation results in one of the following formats.

12.4.3.1 Calculate the void ratio as follows:

$$e = e_o - \frac{\Delta H}{H_s}$$

12.4.3.2 Alternatively, calculate the vertical strain, in percent, as follows:

$$\epsilon = \frac{\Delta H}{H_o} \times 100$$

12.4.4 Calculate the vertical stress as follows:

$$\sigma_v = \frac{P}{A}$$

where:

P = applied load in N

σ_v = vertical stress in kPa.

12.4.5 Referring to Fig. 4, plot the deformation results (void ratio or strain) corresponding to the end of each increment and, if using Test Method B, corresponding to the end-of-primary consolidation versus the logarithm of the pressure.

NOTE 15—In some cases, it may be preferable to present the load-deformation curve in arithmetic scale.

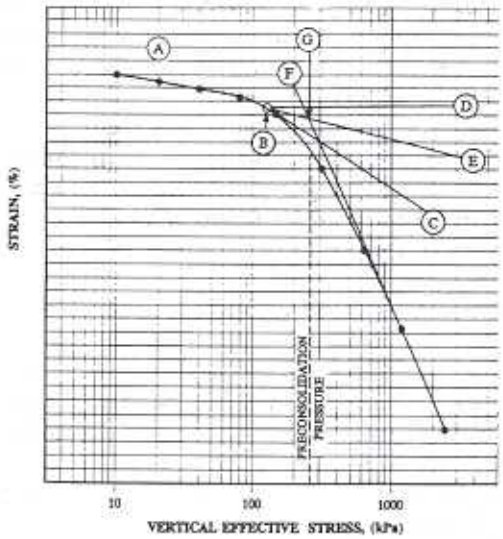


FIG. 4 Evaluation for Preconsolidation Pressure From Casagrande Method

12.4.6 Referring to Fig. 4, determine the value of the preconsolidation pressure using the following procedure.

NOTE 16—Any other recognized method of estimating preconsolidation pressure (see references) may also be used, provided the method is identified in the report.

12.4.6.1 Estimate the point of maximum curvature on the consolidation curve (**B**).

12.4.6.2 Draw the tangent to the consolidation curve at this point (**C**), and a horizontal line through the point (**D**), both extended towards increasing values on the abscissa.

12.4.6.3 Draw the line bisecting the angle between these lines (**E**).

12.4.6.4 Extend the tangent to the steep, linear portion of the consolidation curve (virgin compression branch) (**F**) upwards to intersection with the bisector line (**E**). The pressure (**G**) (abscissa) corresponding to this point of intersection is the estimated preconsolidation pressure.

12.4.7 Complete evaluation often includes consideration of information not generally available to the laboratory performing the test. For this reason further evaluation of the test is not mandatory. Many recognized methods of evaluation are described in the literature. Some of these are discussed in the Refs. (**1**) through (**8**).[3]

13. Report

13.1 In addition to project name and location, boring number, sample number, and depth, report the following information.

13.1.1 Description and classification of the soil in accordance with Practice D 2488 or Test Method D 2487 when Atterberg limit data are available. Specific gravity of solids, Atterberg limits and grain size distribution shall also be reported when available plus the source of such information if other than measurements obtained on test specimen. Also note occurrence and approximate size of isolated large particles.

13.1.2 *Soil Condition*:

13.1.2.1 Average water content of trimmings,

13.1.2.2 Initial and final water content of specimen,

13.1.2.3 Initial and final dry unit weight of specimen,

13.1.2.4 Initial and final void ratio of specimen,

13.1.2.5 Initial and final degree of saturation of specimen, and

13.1.2.6 Preconsolidation pressure.

13.1.3 *Test Procedure*:

13.1.3.1 Preparation procedure used relative to trimming; state whether the specimen was trimmed using a trimming turntable, trimmed using a cutting shoe, or tested directly in a ring from a ring lined sampler.

13.1.3.2 Condition of test (natural moisture or inundated, pressure at inundation).

13.1.3.3 Method of testing (A or B).

13.1.3.4 Test Method used to compute coefficient of consolidation.

13.1.3.5 Listing of loading increments and decrements, and load increment duration, if differing from 24 h; end of increment deformation results and, for Test Method B, end-of-primary deformation results and coefficient of consolidation (see Fig. 1).

13.1.3.6 All departures from the procedure outlined, including special loading sequences.

13.1.4 *Graphical Presentations*:

13.1.4.1 Graph of deformation versus log time (see Fig. 2) or square root of time (see Fig. 3) for those load increments where time rate readings were taken.

13.1.4.2 Graph of void ratio versus log of pressure curve or percent compression versus log of pressure curve (see Fig. 4).

13.1.4.3 In cases where time rate of deformation readings have been taken for several load increments, prepare a graph of the log of coefficient of consolidation versus average void ratio or average percent compression for the respective load increments (see Fig. 5). Alternatively, a graph of coefficient of consolidation or log of coefficient of consolidation versus log of average pressure may be used. If time rate readings were obtained for only two load increments, simply tabulate the values of c_v versus the average pressure for the increment.

NOTE 17—The average pressure between two load increments is chosen because it is a convenient coordinate for plotting the result. Unless the rate of pore pressure dissipation is measured, it is not possible to determine the actual effective pressure at the time of 50 % consolidation. Furthermore, some ambiguity may arise in cases where the test has been carried through one or more intermediate load-rebound cycles.

14. Precision and Bias

14.1 *Statement of Precision*—Due to the nature of the soil materials tested by this test method it is either not feasible or too costly at this time to produce multiple specimens which have uniform physical properties. Any variation observed in the data is just as likely to be due to specimen variation as to operator or laboratory testing variation. Subcommittee D18.05 welcomes proposals that would allow for development of a valid precision statement.

14.2 *Statement of Bias*—There is no acceptable reference value for this test method, therefore, bias cannot be determined.

15. Keywords

15.1 compressibility; compression curves; consolidation; consolidation coefficient; consolidation test; consolidometer; preconsolidation pressure; primary consolidation; rebound; secondary compression; settlement; swelling

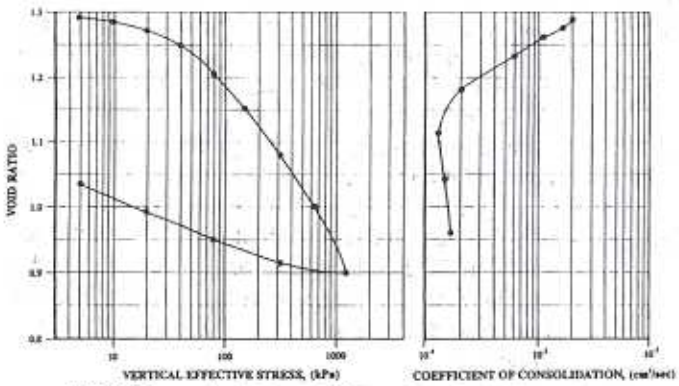


FIG. 5 Example of Consolidation Test Summary Plots

[3] The boldface numbers in parentheses refer to a list of references at the end of the text.

REFERENCES

(1) Casagrande, A., "The Determination of the Pre-Consolidation Load and its Practical Significance," Proceedings 1st ICSMFE, III, 1936, p. 60.
(2) Taylor, D. W., *Fundamentals of Soil Mechanics*, John Wiley and Sons, New York, NY, 1948.
(3) Burmeister, D. M. "The Application of Controlled Test Methods in Consolidation Testing," ASTM STP 126, p. 83, ASTM 1951.
(4) Schmertmann, J. H. "The Undisturbed Consolidation Behavior of Clay" Trans. ASCE, 120, pp. 1201 through 1233, 1955.
(5) Leonards, G. A. "Engineering Properties of Soils," Chapter 2 in *Foundation Engineering* by Leonards, G. A., ed. McGraw-Hill, New York, NY, 1962.
(6) Winterkorn, H. F. and Fang, H. Y. eds. *Foundation Engineering Handbook*, Chapter 4, Von Nostrand Reinhold Co, New York, NY, 1975.
(7) Holtz, R. D. and Kovacs, W. D. *An Introduction to Geotechnical Engineering*, Prentice Hall, Englewood Cliffs, NJ, 1981.
(8) Yong, R. N. and Townsend, F. C. Eds." Consolidation of Soils: Testing and Evaluation," *ASTM STP 892*, ASTM, 1986.

SUMMARY OF CHANGES

This section identifies the principal changes to this test method that have been incorporated since the last issue.

(1) Practice D 3740 has been added to the Section 2 on Referenced Documents.

(2) A new Note 3 was inserted to Reference D3740, and all subsequent notes have been renumbered.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

Appendix 22

SOP – Decontamination Procedures

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Decontamination Procedures

I. Scope and Application

This standard operating procedure describes decontamination protocols to be followed during the treatability study program outlined in the Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck & Lee, Inc. [BBL], 2003a). The treatability studies program will generally follow the decontamination protocols presented in Section B2.4.2 of the SSAP and BMP QAPPs, except for the plate and frame and multimedia filter (MMF) test apparatus. In general accordance with Section B2.4.2 of the SSAP and BMP QAPPs, all non-disposable equipment that comes in contact with samples will be decontaminated prior to initial use, prior to reuse, and at the completion of activities. Decontamination will consist of:

1. Wash with laboratory grade detergent.
2. Rinse with distilled water.
3. Rinse with acetone and allow to dry (contain rinsate for appropriate disposal).
4. Rinse with hexane and allow to dry (contain rinsate for appropriate disposal).
5. Rinse with distilled water.

Decontamination protocols for the pilot-scale plate and frame and MMF test apparatus are described below. Other test-specific decontamination procedures that derive from the steps listed above may be developed based on input from the treatability studies laboratories.

II. Equipment List

The follow materials will be available, as required, during decontamination procedures:

- Personal protective equipment (as required in the *Revised Health and Safety Plan* (Revised HASP) (BBL, 2003b);
- Tap water;
- High-pressure washing equipment; and
- Backwashing equipment.

III. Health and Safety Considerations

Refer to the Revised HASP (BBL, 2003).

IV. Test-Specific Decontamination Procedures

Plate and Frame Test: Due to the size of the plate and frame test apparatus, the decontamination procedure for this piece of equipment has been modified to replace the steps listed in Section I above with the following:

1. Remove the filter media.
2. Clean the test apparatus using high-pressure wash equipment.

Multimedia Filter Tests: Due to the size of the columns used in these tests, the decontamination procedure for this piece of equipment has been modified to replace the steps listed in Section I above with the following:

1. Backwash the column media to 200% expansion (8 feet) for a period of 10 minutes.

All decontamination liquid and other residuals (filter media, disposable health and safety equipment, etc.) will be contained and properly disposed of in accordance with the *Sediment Sampling and Analysis Program Quality Assurance Project Plan* (SSAP QAPP) (Environmental Standards, Inc. [ESI] and Quantitative Environmental Assessment [QEA], 2002).

V. References

BBL. 2003a. *Treatability Studies Work Plan*. Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

BBL. 2003b. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

ESI and QEA. 2002. *Sediment Sampling and Analysis Program Quality Assurance Project Plan* (SSAP QAPP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY

Appendix 23

SOP – Sample Handling and Custody Requirements

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Standard Operating Procedure: Sample Handling and Custody Requirements

I. Scope and Application

This standard operating procedure (SOP) presents sample handling and custody protocols to be followed during activities described in the Treatability Studies Work Plan (TS Work Plan) (Blasland, Bouck, & Lee, Inc. [BBL], 2003a) and includes collection of sediment and water samples, transfer of these samples to a field laboratory for processing, transfer to one or more treatability studies laboratories for testing, and submission of sediment, water, and treatment residuals samples for laboratory analysis. The protocols described herein generally follow the procedures outlined in the *Sediment Sampling and Analysis Program Quality Assurance Project Plan* (SSAP QAPP) (Environmental Standards, Inc., [ESI] and Quantitative Environmental Assessment [QEA], 2002) and *Baseline Monitoring Program Quality Assurance Project Plan* (BMP QAPP), (QEA and ESI, 2003).

The primary objective of sample custody procedures is to create an accurate written record which can be used to trace the possession and handling of samples from collection, through processing, testing, and analysis, and ultimately their disposition.

II. Health and Safety Considerations

Refer to the *Revised Health and Safety Plan* [Revised HASP]) (BBL, 2003b).

III. Field Sample Handling and Custody Requirements

1. General

Field sample handling and custody protocols will be implemented during sediment and water sample collection activities and sample processing in the field laboratory (described in Appendix 1 – SOP for Sample Collection for Treatability Testing and Appendix 2 – SOP for Dredged Material Slurry Simulations, respectively). A field notebook will be used to document custody and other pertinent information (as described below and in other SOPs) during these activities. The original field notebook will be maintained in the project file (as described in Appendix 30 of the TS Work Plan), and a copy of the field notebook will be maintained on file at the field laboratory. The Treatability Studies Coordinator or field personnel are responsible for documenting each sample transfer and maintaining custody of samples until they are shipped, or delivered by courier, to the laboratory or disposed.

2. Sediment Core Sampling

Upon collection of an acceptable sediment core, the core will be capped, sealed, and labeled per the protocols specified in Appendix 1 of the SSAP QAPP – SOP for Sediment Collection and Appendix 1 of this TS Work Plan. Each core will be marked, using a permanent marker, with an arrow to show the top of the core, and labeled with the sampling location, and the date and time of core collection. The capped cores will be maintained in a vertical position aboard the sampling vessel until the end of the day when they are transmitted to the field laboratory for processing. Custody of the sediment cores during sample collection and field transfer activities will be documented in the field notebook. At minimum, the field notebook will document the following for each core:

- Field sample identification number;
- Date and time collected;
- Northing and easting of sample location;
- Depth of water at sample location;
- Core penetration depth (in);
- Custodian's initials;
- Sediment category; and
- Observations, including probing results and presence of odor.

3. Surface Water Sampling

Water samples will be collected in accordance with the protocols presented in Appendix 2 of the TS Work Plan. Samples will be collected in appropriately sized containers. After a sample has been collected, a self-adhesive, waterproof label will be affixed to each container. At a minimum, the label will contain:

- Field sample identification number;
- Date and time collected;
- Sample location;
- Depth of water at sample location; and
- Custodian's initials.

At the conclusion of sampling activities for the day, the water samples will be transferred to the field laboratory. Custody of the water samples during collection and field transfer activities will be documented in the field notebook. At minimum, the field notebook will document the following for each water sample:

- Field sample identification number;
- Date and time collected;
- Sample location;
- Depth of water at sample location;
- Custodian's initials;
- Field parameters (temperature, pH, dissolved oxygen, etc., per Appendix 2); and
- Observations.

4. Field Processing Laboratory

Processing activities will include collecting baseline samples specified in the TS Work Plan and preparing and storing the dredged material slurry simulations per the protocols presented in Appendix 2 to the TS Work Plan. Processing activities will be documented in the field notebook.

In general conformance with Appendix 1 of the SSAP QAPP, all necessary sample containers will be shipped or delivered by laboratory courier to the sediment sample processing facility and received by the Treatability Studies Coordinator or field personnel. Sample containers meeting EPA cleaning requirements may be purchased by GE and shipped directly to the site due to the volume of sample containers needed. Under this condition, certificates of analysis documenting the bottle cleanliness will be filed at the sample processing facility. Anticipated sample container and preservation requirements are presented in Table 7. The laboratory(ies) or bottle vendor will deliver containers on a periodic basis to the facility such that an adequate supply of sample containers exists for several days. A laboratory supplied and initialed Chain-of-Custody (COC) will be used to document preparation and delivery of sample containers to the site. The Treatability Studies Coordinator will terminate this container delivery COC upon receipt at the site and copies will be filed in the sample processing laboratory records. Sample containers needed for a specific sampling task will then be relinquished by Treatability Studies Coordinator (or designate) to the field processing team after verifying the integrity of the containers and confirming that the proper bottles have been assigned for the task to be conducted.

After a given sample or slurry has been prepared, a self-adhesive, waterproof label will be affixed to each container. At a minimum, the label will contain:

- Field sample identification number,
- Date and time collected,
- Custodian's initials, and
- Analysis, or treatability tests to be performed.

Immediately after sample/slurry preparation and labeling, each container designated for analysis or treatability testing will be sealed into a plastic bag and placed into an insulated cooler with "wet ice" or icepacks (for samples requiring temperature preservation) and appropriate packing materials for shipment to the laboratory. Slurry preparations may also be stored consistent with the protocols presented in Attachment 2 to the TS Work Plan.

A field COC record will accompany all samples/slurries shipped from the processing laboratory to their destination. An example of the field COC records is provided as Attachment 1. Field COC records may be prepared either using a computerized sample tracking and COC program that will be integral to the project database or via hand or preprinted COC forms.

The field laboratory personnel will properly relinquish the samples/slurry preparations on the field COC record. These record forms will be sealed in a plastic bag to protect them against moisture. Sample volumes collected for matrix spike (MS) and matrix spike duplicate (MSD) analysis will be noted on the chain-of-custody forms, and the associated additional sample containers will be labeled with the appropriate suffix (MS or MSD). Field duplicates will be designated and shall otherwise be in no way distinguishable by the laboratory as duplicate samples. Rinse blanks will be identified on the COC. The temperature of a temperature bottle blank will be monitored to ensure all samples requiring temperature preservation are within $4° \pm 2°$ Celsius (C), as required, prior to leaving the field laboratory.

Temperature blanks will consist of bottles filled with distilled or tap water. The shipping coolers (or other appropriate containers) will then be sealed utilizing custody seals that will be initialed by the Treatability Studies Coordinator or designate. All sample coolers (or other appropriate containers) will be delivered to the

analytical or treatability laboratory by direct courier or other appropriate shipment method at the end of each day's processing activities.

IV. Analytical/Treatability Laboratory Sample Receipt and Custody Requirements

Following sample/slurry preparation receipt, the laboratory will be responsible for checking the samples/slurry preparations and maintaining the samples/slurry preparations in general conformance with Section B3.2 of the SSAP QAPP, and SOPs associated with the treatability study program. The laboratory shall verify receipt of the samples electronically (via e-mail) on the following day. The laboratory will maintain custody of the samples/slurry preparations until they are shipped or delivered by courier to another laboratory, archived, or disposed.

In conformance with SSAP QAPP procedures, once samples are received at the laboratory, the field COC record is completed and signed by the individual laboratory receipt personnel. Laboratory receipt personnel will check the labels against the corresponding information listed on the field COC records and note any discrepancies. Additionally, the laboratory sample receipt personnel will note any damaged or missing sample containers. Any discrepancies in sample identifications, sample analysis information, or any indication that samples are missing upon receipt at the laboratory will be communicated to the QA Manager within 24 hours of sample receipt so that appropriate corrective action can be determined and implemented.

After the sample receipt information is checked and recorded, sample analysis information will be entered into the individual Laboratory Information Management System (LIMS) (or equivalent). Each sample will be provided a unique laboratory identification number and the analysis tests requested on the COC records will be entered into the LIMS. After the required information has been entered into the LIMS, laboratory personnel will initiate an internal laboratory COC. The internal COC will document the transfer of samples from the storage location to the analyst for analysis and subsequently through archiving or final disposition at the laboratory, or transfer to a subsequent laboratory. At a minimum, the internal COC will include client identification, laboratory sample number, sample matrix, signatures for relinquishing and receiving samples, and reasons for the change in custody (procedure to be performed).

Samples transferred to subsequent laboratories will be under the custody procedures described in Section IV above, or an approved equivalent.

V. Extract and Sample Archive Procedures

Samples extracts from all the laboratory analytical procedures will be held frozen (-10° C) for a period of one month following receipt of the final data packages. It is not anticipated that treatability studies samples, slurry preparations, or sediment and water samples will be archived during the treatability studies program.

VI. References

BBL. 2003b. *Revised Health and Safety Plan* (Revised HASP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

BBL. 2003a. *Treatability Studies Work Plan* (TS Work Plan). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

ESI and QEA. 2002. *Sediment Sampling and Analysis Program - Quality Assurance Project Plan* (SSAP-QAPP). Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

QEA and ESI. 2003. *Baseline Monitoring Program Quality Assurance Project Plan* (BMP QAPP) Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY.

Attachment 1

Sample Chain of Custody

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

BBL
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

6723 Towpath Road, P.O. Box 66
Syracuse, New York 13214-0066
TEL: (315) 446-9120

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME					Number of Containers							
SAMPLERS: *(Signature)*													
STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION								REMARKS

Relinquished by: *(Signature)*	DATE	TIME	**Received by:** *(Signature)*	**Relinquished by:** *(Signature)*	DATE	TIME	**Relinquished by:** *(Signature)*	
Relinquished by: *(Signature)*	DATE	TIME	**Received by:** *(Signature)*	**Relinquished by:** *(Signature)*	DATE	TIME	**Relinquished by:** *(Signature)*	
Relinquished by: *(Signature)*	DATE	TIME	**Received for Laboratory by:** *(Signature)*	DATE	TIME	**Remarks:**		

10/23/95
5951188L.CDR

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

Appendix 24

SOP – Data Management Plan

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

Appendix 24: Data Management Plan

The purpose of the data management plan is to ensure that all of the necessary data are accurate and readily accessible to meet the analytical and reporting objectives of the project. The treatability studies program will encompass a large number of samples and analytes from a variety of different treatability tests. From the large amount of resulting data, the need arises for a structured, comprehensive, and efficient program for management of data.

The data management program established for the project includes field documentation and sample QA/QC procedures, methods for tracking and managing the data, and a system for filing all site-related information. More specifically, data management procedures will be employed to efficiently process the information collected such that the data are readily accessible and accurate. These procedures are described in detail in the following section.

The data management plan has five elements: 1) sample designation system, 2) field activities, 3) sample tracking and management, 4) data management system, and 5) document control and inventory.

1.1 Sample Designation System

A concise and easily understandable sample designation system is an important part of the project sampling activities. It provides a unique sample number that will facilitate both sample tracking and easy re-sampling of select locations to evaluate data gaps, if necessary. The sample designation system to be employed during the treatability studies activities will be developed with input from the selected treatability studies laboratory(ies). The sample designation system will be consistent, yet flexible enough to accommodate unforeseen sampling events or conditions. A combination of letters and numbers will be used to yield a unique sample number for each field sampled collected, as outlined below.

1.2 Field Activities

Field activities designed to gather the information necessary to make decisions regarding the treatability studies results require consistent documentation and accurate record keeping. During treatability studies activities, standardized procedures will be used for documentation of field activities, data security, and QA. These procedures are described in further detail in the following subsections

1.2.1 Field and Treatability Laboratory Documentation

Complete and accurate record keeping is a critical component of the treatability studies activities. When interpreting analytical results and identifying data trends, investigators realize that field notes are an important part of the review and validation process. To ensure that the field investigation is thoroughly documented, several different information records, each with its own specific reporting requirements, will be maintained, including:

- Field notebooks;
- Treatability test observation notes; and

- Chain-of-custody forms.

A description of each of these types of field documentation is provided below.

Field Notebooks

The personnel performing the field activities will keep field notebooks that detail observations and measurements made during the sample collection and processing activities, per the protocols in Appendix 1 – SOP for Sample Collection Procedures. Data will be recorded directly into the field notebooks. Erroneous entries will be corrected by crossing out the original entry, initialing it, and then documenting the proper information.

Treatability Laboratory Notes

The personnel performing the treatability test activities will keep notes that detail observations and measurements made during the treatability studies, per the protocols in the applicable method SOPs. Data will be recorded directly into the field notebooks. Erroneous entries will be corrected by crossing out the original entry, initialing it, and then documenting the proper information.

Chain-of-Custody Forms

COC forms are used as a means of documenting and tracking sample possession from time of collection to the time of disposal. All field and laboratory personnel will be briefed on the proper use of the COC procedure. A more thorough description of the COC forms is presented in Appendix 29 – SOP Sample Handling and Custody Procedures.

1.2.2 Data Security

Measures will be taken during the field investigation to ensure that samples and records are not lost, damaged, or altered. When not in use, field notebooks will be stored at the field office or locked in the field vehicle or secured at the treatability testing facility. Access to these files will be limited to the field personnel who utilize them.

1.3 Sample Management and Tracking

Records of field documentation, as well as analytical and QA/QC results, will be maintained to ensure the validity of data used in the site analysis. To effectively execute such documentation, carefully constructed sample tracking and data management procedures will be used throughout the sampling program.

Sample tracking will begin with the completion of field logbook entries, as described in Appendix 29 – SOP Sample Handling and Custody Procedures. The original field notebook will be maintained in the project file (as described in Appendix 30 of the TS Work Plan), and a copy of the field notebook will be maintained on file at the field laboratory.

COCs for samples and slurry preparations shipped to the treatability and analytical laboratory(ies) will be competed as described in Appendix 29 – SOP Sample Handling and Custody Procedures. On a daily basis, the completed forms associated with samples shipped and/or collected that day will be faxed to the QA Manager. Copies of completed forms will be maintained in the project file.

The treatability/analytical laboratory shall verify receipt of the samples electronically (via email) on the following day. When analytical data and/or treatability study results are received from the laboratory, the QA Manager will review the incoming analytical data packages against the information on the COCs to confirm that the correct analyses were performed for each sample and that results for all samples submitted for analysis were received. Any discrepancies noted will be promptly followed-up by the QA Manager.

1.4 Data Management System

In addition to the sample tracking system, a data management system will be implemented. The central focus of the data management system will be the development of a personal computer-based project database. The project database, to be maintained by the BBL, will combine pertinent geographical, field, treatability test, and analytical data. Information that will be used to populate the database will be derived from four primary sources: surveying of sampling locations, field observations, treatability test observations and results, and analytical results. Each of these sources is discussed in the following sections.

1.4.1 Computer Hardware

The database will be constructed on Pentium™-based personal computer work stations connected through a Novell network server (or equivalent). The network system will provide access to various hardware peripherals, such as laser printers, backup storage devices, image scanners, modems, etc. Computer hardware will be upgraded to industrial and corporate standards, as necessary, in the future.

1.4.2 Computer Software

The database will be written in Microsoft Access, running in a Windows operating system. Custom applets, such as diskette importing programs, will be written in either Microsoft VBA or Microsoft Visual Basic. Geographic Information System (GIS) applications will be developed in ESRI ArcGIS, with additional customization performed with Visual Basic. Tables and other database reports will be generated through Access in conjunction with Microsoft Excel, Microsoft Word, and/or Seagate Crystal Reports. These software products will be upgraded to current industrial standards, as necessary.

1.4.3 Survey Information

In general, each location sampled as part of the treatability testing program will be surveyed to ensure accurate documentation of sample locations for mapping and GIS purposes, to facilitate the re-sampling of select sample locations during future monitoring programs, if needed, and for any additional activities. The surveying activities that will occur in the field will follow the protocols established in the SSAP QAPP.

Following the approval of the computed information, the coordinates and elevations will be transferred to the BBL both in a digital and a hard copy format. This data will then be loaded into the database and linked to the field and analytical data.

1.4.4 Field Observations and Treatability Study Observations

An important part of the information that will ultimately reside in the data management system for use during the project will originate in the observations that are recorded in the field and during the treatability studies.

Following each sampling event, a status memorandum will be prepared by the field personnel who performed the sampling activities. Likewise, following each treatability study, a status memorandum will be prepared by the personnel who performed the treatability study activities. The purpose of the status memorandum is to present a summary and a record of the event. Topics to be discussed include the locations sampled, the sampling/testing methodologies used, QA/QC procedures, blind duplicate and MS/MSD sample identification numbers, equipment decontamination procedures, personnel involved in the activity, and any other noteworthy events that occurred.

Status memorandum are tools used to keep project personnel informed on the details of the field and treatability study activities and are also invaluable during the development of the final report. Each status memorandum will be reviewed for accuracy and completeness by the respective sampling activity manager. Following the approval and finalization of each memorandum, the status memorandum will be used to transfer field observations into the data management system.

1.4.5 Analytical Results

Analytical results will be provided by the laboratory in both a digital and a hard copy format (full, CLP-equivalent data packages). Upon receipt of each analytical package, the original COC form will be placed in the project files. The data packages will be examined to ensure that the correct analyses were performed for each sample submitted and that all of the analyses requested on the COC form were performed. If discrepancies are noted, the QA Manager will be notified and will promptly follow up with the laboratory to resolve any issues.

Each data package will be validated in accordance with the procedures presented in Section 3.3 of the *Treatability Studies Work Plan* (BBL, 2003). Any data that does not meet the specified standards will be flagged pending resolution of the issue. The flag will not be removed from the data until the issue associated with the sample results is resolved. Although flags may remain for certain data, the use of that data may not necessarily be restricted.

Following completion of the data validation, the digital files will be used to populate the appropriate database tables. An example of the electronic data deliverable (EDD) format is included in Attachment 1. This format specifies one data record for each constituent for each sample analyzed. Specific fields include:

- Sample identification number;
- Date sampled;
- Date analyzed;
- Parameter name;
- Analytical result;
- Units;
- Detection limit; and
- Qualifier(s).

The individual EDDs, supplied by the laboratory in either an ASCII comma separated value (CSV) format or in a Microsoft Excel worksheet, will be loaded into the appropriate database

table via a custom-designed user interface Visual Basic program. Any analytical data that cannot be provided by the laboratory in electronic format will be entered manually. After entry into the database, the EDD data will be compared to the field information previously entered into the database to confirm that all requested analytical data have been received.

1.4.6 Data Analysis and Reporting

The database management system will have several functions to facilitate the review and analysis of the treatability study data. Routines have been developed to permit the user to scan analytical data from a given site for a given media. Several output functions are also available which can be modified, as necessary, for use in the data management system.

A valuable function of the data management system will be the generation of tables of analytical results from the project databases. The capability of the data management system to directly produce tables reduces the redundant manual entry of analytical results during report preparation and precludes transcription errors that may occur otherwise. This data management system function creates a digital file of analytical results and qualifiers for a given media. The file can then be processed into a table of rows and columns which can be transferred to word processing software (e.g., Microsoft Word) for final formatting and addition of titles and notes. Tables of analytical data will be produced as part of data interpretation tasks and the reporting of data to USEPA.

Another function of the data management system will be to create digital files of analytical results and qualifiers suitable for transfer to mapping/presentation software. A function has been created by BBL that creates a digital file consisting of sample location number, state plane coordinates, sampling date, and detected constituents and associated concentrations and analytical qualifiers. The file is then transferred to an AutoCAD work station, where another program has been developed to plot a location's analytical data in a "box" format at the sample location (represented by the state plane coordinates). This routine greatly reduces the redundant keypunching of analytical results and facilitates the efficient production of interpretative and presentation graphics.

The data management system also has the capability of producing a digital file of select parameters that exists in one or more of the databases. This type of custom function is accomplished on an interactive basis and is best used for transferring select information into a number of analysis tools, such as statistical or graphing programs.

1.4.7 Document Control and Inventory

BBL maintains project files in its Syracuse, New York office. Each client project is assigned a file/job number. Each project file is then organized into the following subfiles:

File Number	File Name	Contents
#1	Agreements/Proposals	Subcontractor Agreements, Client Contracts, Proposals, Letter Proposals
#2	Change Orders/Purchase Orders	Change Orders, Purchase Orders, Work Variances
#3	Invoices	Invoices, Invoice Cover Letters, Subcontractor Invoices
#4	Project Management	Project Plan, Organizational Charts, Team Directories, Mailing Lists, Project Schedules, Calendars
#5	Correspondence	Letters, Agency Letters, Client Correspondence,

		Subcontractor Correspondence, Memos, Meeting Minutes, Agendas, Phone Logs, E-Mails, Conversation Records
#6	Notes and Data	Daily Logs, Field Notes, Site Photographs, Analytical Data and Tables, Drawings, Blue Prints, Modeling Data, GIS Output, Surveying Info
#7	Public Relations Information	Newspaper Clippings, Press Releases, Community Newsletters, Web Articles
#8	Regulatory Documents	Permit Applications, Permits, Records of Decision (RODs), Consent Decrees, Administrative Orders of Consent (AOCs), Unilateral Administrative Orders (UAOs), Statements of Work (SOWs), Federal Registers
#9	Marketing Documents	Marketing Brochures, Marketing Letters, Qualifications
#10	Final Reports/Presentations	Final Reports and Presentations produced by BBL.
#11	Draft Reports/Presentations	Draft Reports and Presentations (works in progress) produced by BBL.
#12	Documents Prepared by Others	Draft and Final Reports, Presentations, and other Documents produced by another organization, such as Agencies, Clients, Subcontractors, and other Organizations

Originals, when possible, are placed in the files. These are the central files and will serve as the site-specific files for the off-site investigations.

Attachment 1

Electronic Data Deliverable Format

EDD Field Definitions

Field Name	Data Type	Notes
Sample Name	Text-50	Sample ID as it appears on Laboratory Form 1 for analysis (ex: MW-1 reported as MW-1RE for re-analysis).
COC Sample Name	Text-50	Sample ID as it appears on the chain of custody.
SDG	Text-50	Sample Delivery Group
Lab Sample ID	Text-50	
Matrix	Text-10	ex: Soil, Water, Sediment
Sample Type	Text-10	ex: FB, RB, FD , FS -- for Field Blank, Rinse Blank, Field Duplicate, Field Sample, respectively.
Date Collected	Date/Time	
Time Collected	Date/Time	
Depth Start	Number	
Depth End	Number	
Depth Units	Text-25	
Method	Text-50	Analytical method used by laboratory
CAS Number	Text-25	
Analyte	Text-100	
Result Value	Number	For non-detected results, enter Reporting Limit and "U" must be present in Lab Qualifiers field.
Lab Qualifiers	Text-10	"U" for not detected, others as defined by the lab.
Reporting Limit	Number	
Result Units	Text-25	
Dilution Factor	Number	
Reportable Result	Yes/No	If not included, default on import will be "Yes". Used where re-analyses or dilutions are present to determine proper result to report.
Filtered	Yes/No	
MDL	Number	Method Detection Limit
Date Analyzed	Date/Time	
Time Analyzed	Date/Time	
Date Received	Date/Time	Date Received by Lab
Laboratory	Text-50	
Lab Certification Number	Text-50	

Number after "Text-" indicates the maximum number of characters allowed.

Fields highlighted in pink are not required. They may be left empty or field can be eliminated from EDD if lab is not providing that data.

If lab is providing Matrix or Sample Types, they can use codes different from the examples above but will need to provide definitions for them

Lab QC samples should not be included on EDD (lab blanks, lab replicates, etc.). Only samples from chain of custody should be included

Depth Related fields can be left blank for samples where they are not applicable

Appendix 25

SOP – BOD5 (USEPA 405.1)

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD #: 405.1	Approved for NPDES (Editorial Revision 1974)
TITLE:	Biochemical Oxygen Demand (5 Days, 20°C)
ANALYTE:	BOD Biological Oxygen Demand
INSTRUMENTATION:	Probe
STORET No.	00310 Carbonaceous 80082

1.0 Scope and Application

1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological populationwater movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

2.0 Summary of Method

2.1 The sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

3.0 Comments

3.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.

3.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).

3.3 The use of 60 mL incubation bottles in place of the usual 300 mL incubation bottles, in conjunction with the probe, is often convenient.

4.0 Precision and Accuracy

4.1 Eighty-six analysts in fifty-eight laboratories analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 2.1 and

175 mg/L BOD, the standard deviation was ±0.7 and ±26 mg/L, respectively (EPA Method Research Study 3).

4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

5.0 References

5.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 15th Edition, p.83, Method 507 (1980).

5.2 Young, J. C., "Chemical Methods for Nitrification Control," J. Water Poll. Control Fed., 45, p. 637 (1973).

Appendix 26

SOP – pH (EPA 9040B/9041A/9045C) (sediment analysis)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD 9040B

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2 The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (<0.1 molar solution) salinity.

3.2 Sodium error at pH levels >10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer and/or temperature sensor for automatic compensation.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2

for acidic wastes and a pH 12 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25±1°C if the pH of the waste is above 12.0.) Various instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (<0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive aliquots of sample until values differ by <0.1 pH units. Two or three volume changes are usually sufficient.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.

8.2 Electrodes must be thoroughly rinsed between samples.

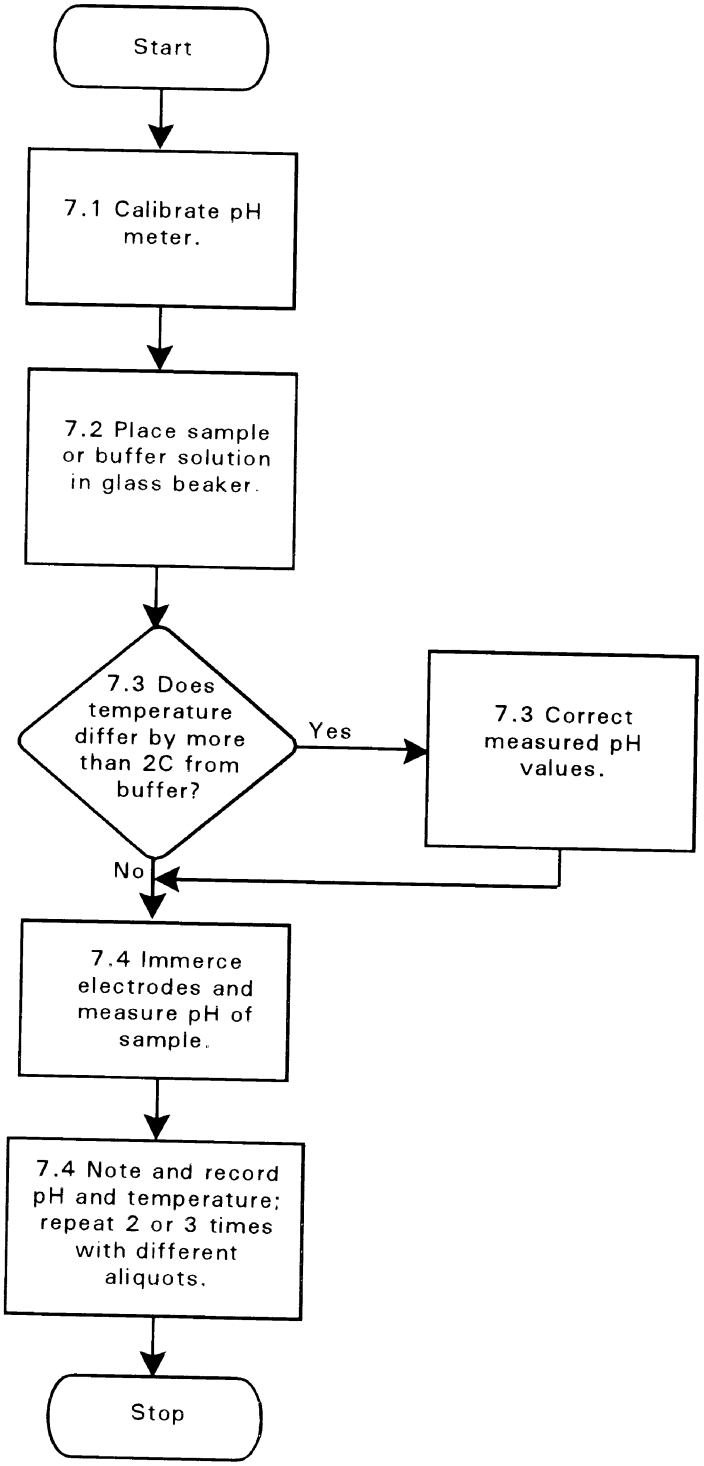
9.0 METHOD PERFORMANCE

9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

		Accuracy as	
	Standard Deviation	Bias	Bias
pH Units	pH Units	%	pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

10.0 REFERENCES

1. National Bureau of Standards, Standard Reference Material Catalog 1986-87, Special Publication 260.


Start
7.1 Calibrate pH meter.
7.2 Place sample or buffer solution in glass beaker.
7.3 Does temperature differ by more than 2C from buffer?
Yes
7.3 Correct measured pH values.
No
7.4 Immerce electrodes and measure pH of sample.
7.4 Note and record pH and temperature; repeat 2 or 3 times with different aliquots.
Stop

METHOD 9041A

pH PAPER METHOD

1.0 SCOPE AND APPLICATION

1.1 Method 9041 may be used to measure pH as an alternative to Method 9040 (except as noted in Step 1.3) or in cases where pH measurements by Method 9040 are not possible.

1.2 Method 9041 is not applicable to wastes that contain components that may mask or alter the pH paper color change.

1.3 pH paper is not considered to be as accurate a form of pH measurement as pH meters. For this reason, pH measurements taken with Method 9041 cannot be used to define a waste as corrosive or noncorrosive (see RCRA regulations 40 CFR §261.22(a)(1).

2.0 SUMMARY OF METHOD

2.1 The approximate pH of the waste is determined with wide-range pH paper. Then a more accurate pH determination is made using "narrow-range" pH paper whose accuracy has been determined (1) using a series of buffers or (2) by comparison with a calibrated pH meter.

3.0 INTERFERENCES

3.1 Certain wastes may inhibit or mask changes in the pH paper. This interference can be determined by adding small amounts of acid or base to a small aliquot of the waste and observing whether the pH paper undergoes the appropriate changes.

CAUTION: THE ADDITION OF ACID OR BASE TO WASTES MAY RESULT IN VIOLENT REACTIONS OR THE GENERATION OF TOXIC FUMES (e.g., hydrogen cyanide). Thus, a decision to take this step requires some knowledge of the waste. See Step 7.3.3 for additional precautions.

4.0 APPARATUS AND MATERIALS

4.1 Wide-range pH paper.

4.2 Narrow-range pH paper: With a distinct color change for every 0.5 pH unit (e.g., Alkaacid Full-Range pH Kit, Fisher Scientific or equivalent). Each batch of narrow-range pH paper must be calibrated versus certified pH buffers or by comparison with a pH meter which has been calibrated with certified pH buffers. If the incremental reading of the narrow-range pH paper is within 0.5 pH units, then the agreement between the buffer or the calibrated pH meter with the paper must be within 0.5 pH units.

4.3 pH Meter (optional).

5.0 REAGENTS

5.1 Certified pH buffers: To be used for calibrating the pH paper or for calibrating the pH meter that will be used subsequently to calibrate the pH paper.

5.2 Dilute acid (e.g., 1:4 HCl).

5.3 Dilute base (e.g., 0.1 N NaOH).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan which addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 A representative aliquot of the waste must be tested with wide-range pH paper to determine the approximate pH.

7.2 The appropriate narrow-range pH paper is chosen and the pH of a second aliquot of the waste is determined. This measurement should be performed in duplicate.

7.3 Identification of interference:

7.3.1 Take a third aliquot of the waste, approximately 2 mL in volume, and add acid dropwise until a pH change is observed. Note the color change.

7.3.2 Add base dropwise to a fourth aliquot and note the color change. (Wastes that have a buffering capacity may require additional acid or base to result in a measurable pH change.)

7.3.3 The observation of the appropriate color change is a strong indication that no interferences have occurred.

CAUTION ADDITION OF ACID OR BASE TO SAMPLES MAY RESULT IN VIOLENT REACTIONS OR THE GENERATION OF TOXIC FUMES. PRECAUTIONS MUST BE TAKEN. THE ANALYST SHOULD PERFORM THESE TESTS IN A WELL-VENTILATED HOOD WHEN DEALING WITH UNKNOWN SAMPLES.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for easy reference or inspection.

8.2 All pH determinations must be performed in duplicate.

8.3 Each batch of pH paper must be calibrated versus certified pH buffers or a pH meter which has been calibrated with certified pH buffers.

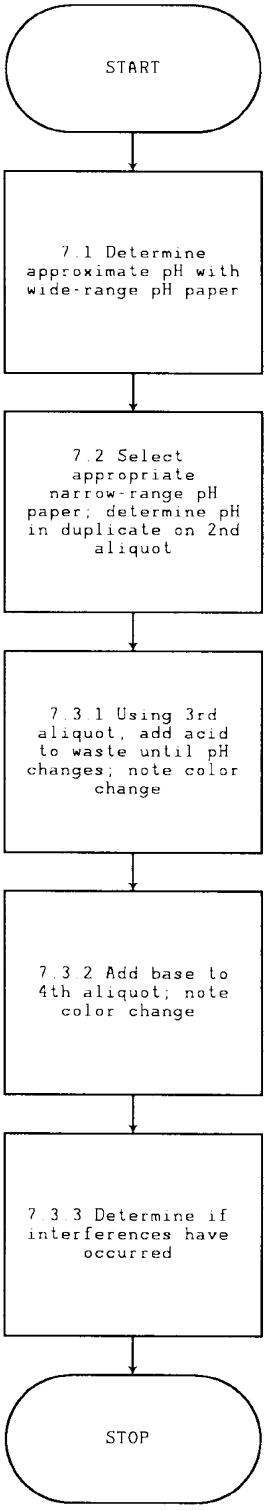
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

pH PAPER METHOD



METHOD 9045C

SOIL AND WASTE pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

2.0 SUMMARY OF METHOD

2.1 The sample is mixed with reagent water, and the pH of the resulting aqueous solution is measured.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacturer's instructions.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Glass Electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

> NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Beaker: 50-mL.

4.5 Thermometer and/or temperature sensor for automatic compensation.

4.6 Analytical balance: capable of weighing 0.1 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.4 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NIST standards, are recommended for routine use.

6.0 SAMPLE PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value. If an accurate pH reading based on the conventional pH scale [0 to 14 at 25°C] is required, the analyst should control sample temperature at 25±1°C when

sample pH approaches the alkaline end of the scale (e.g., a pH of 11 or above).

7.2 Sample preparation and pH measurement of soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. . Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.

7.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or filter or centrifuge off the aqueous phase for pH measurement.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water at __ °C" where "__°C" is the temperature at which the test was conducted.

7.3 Sample preparation and pH measurement of waste materials:

7.3.1 To 20 g of waste sample in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. . Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.

7.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution

in this manner. For combination electrodes, immerse just below the suspension.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "waste pH measured in water at __ °C" where "__°C" is the temperature at which the test was conducted.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.

8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

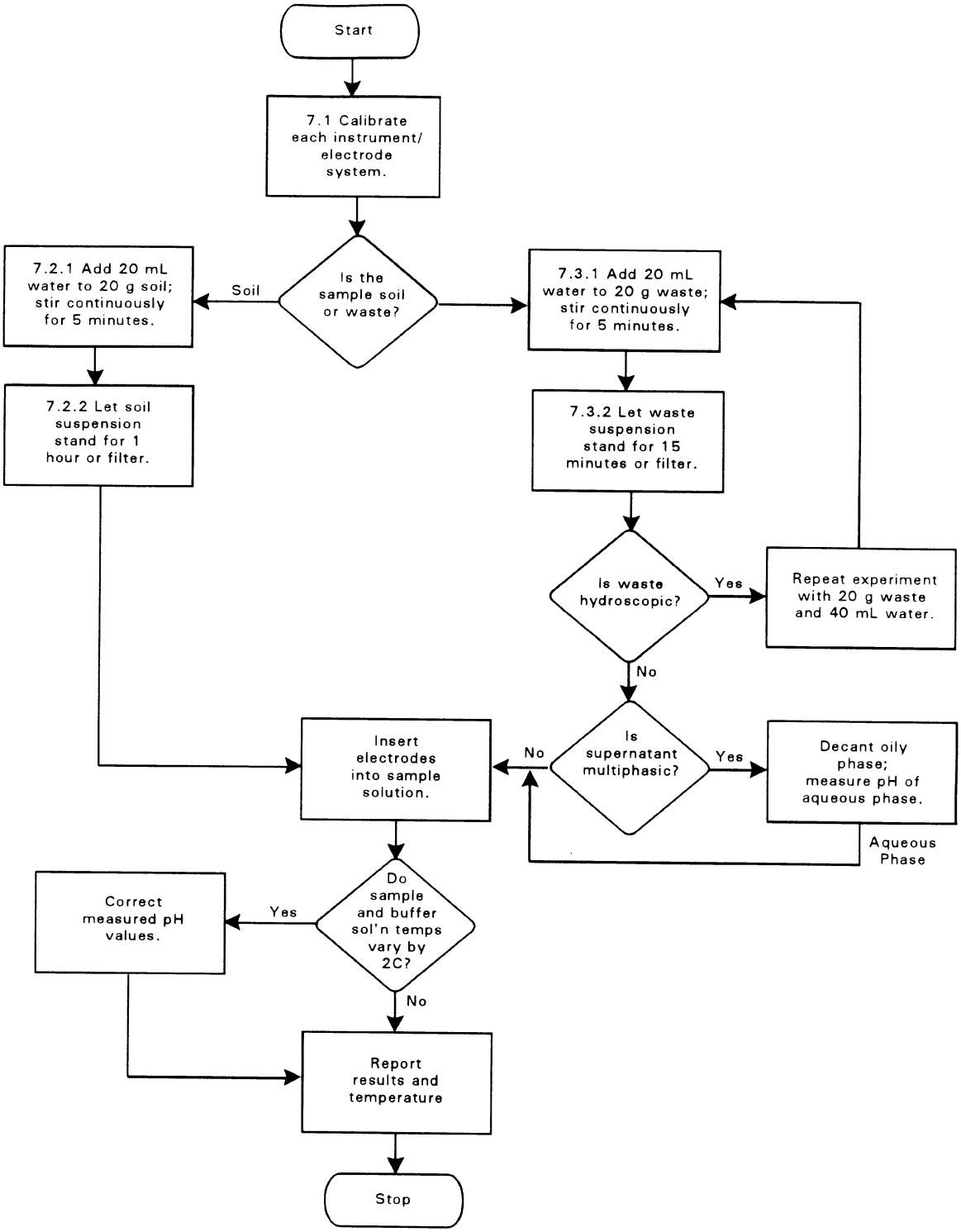
9.1 No data provided.

10.0 REFERENCES

1. Black, Charles Allen; Methods of Soil Analysis; American Society of Agronomy: Madison, WI, 1973.

2. National Bureau of Standards, Standard Reference Material Catalog, 1986-87, Special Publication 260.

SOIL AND WASTE pH



Appendix 27

SOP – PAH (SW-846 Method 8270C/3510C) (sediment/water analysis)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (IS)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (IS)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4-Diaminotoluene	95-80-7	DC,0E(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (IS)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,0S(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (IS)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-n-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (IS)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (IS)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW,0S(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d_{14}(surr)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,O,O-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

IS = This compound may be used as an internal standard.
surr = This compound may be used as a surrogate.
AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (Table 11 contains surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (Table 12 contains performance data), and Method 3561 describes a supercritical fluid extraction of solids for PAHs (see Tables 13, 14, and 15 for performance data).

1.3 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, Method 8270 is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. Refer to Sec. 7.0 of Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.4.6 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.7 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4.8 Toluene diisocyanate rapidly hydrolyses in water (half-life of less then 30 min.). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.9 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer

4.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 3 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria in Table 3 when 5 or 50 ng are introduced.

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.1.6 Guard column (optional) - (J&W Deactivated Fused Silica, 0.25 mm ID x 6 m, or equivalent) between the injection port and the analytical column joined with column joiners (Hewlett-Packard Catalog No. 5062-3556, or equivalent).

4.2 Syringe - 10-µL.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.0001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.3.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.3.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met.

5.4.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1 mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at -10°C or less when not in use. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.4.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at -10°C or less when not in use. If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method.

5.6.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.6.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored at -10°C or less, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration verification standard should be prepared weekly and stored at 4°C. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7 Surrogate standards - The recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

5.7.1 Surrogate Standard Check: Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

5.7.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute surrogate solution may be necessary.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS).

5.8.1 Matrix Spike Check: Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

5.8.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute matrix and LCS spiking solution may be necessary.

5.8.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking

standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Store the sample extracts at -10°C, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

7.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L). Therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of interest	Methods
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620

Analytes of interest	Methods
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene elutes
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

7.3.1.2 Use the DFTPP mass intensity criteria in Table 3 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD

should not exceed 20%. (See Sec. 8.0 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

7.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column. The use of a guard column (Sec. 4.1.6) between the injection port and the analytical column may help prolong analytical column performance.

7.3.2 The internal standards selected in Sec. 5.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation).

7.3.3 Analyze 1-2 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 5.6 and Method 8000). The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

Calculate response factors (RFs) for each target analyte relative to one of the internal standards as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.

7.3.4.2 The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC (see Table 4) must be less than or equal to 30%.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.5.4 If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

7.3.7 Linearity of target analytes - If the RSD of any target analytes is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.7.1 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 in Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 designates a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8270 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000B for method blank performance criteria.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration check compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Table 4 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference for each CCC is less than or equal to 20%, then the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project,

and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1-mL concentrated sample extract obtained from sample preparation.

7.5.3 Inject a 1-2 µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 7.3). The volume to be injected should contain 100 ng of base/neutral and 200 ng of acid surrogates (assuming 100% recovery), unless a more sensitive GC/MS system is being used and the surrogate solution is less concentrated then that listed in Sec. 5.7. The injection volume must be the same volume used for the calibration standards.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/µL, unless a more sensitive GC/MS system is being used).

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. However, SIM

may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be identified, quantitated and reported as the sum of both compounds by the GC.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the

analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (Sec. 7.3.5). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, by Methods 8081 or 8082. However, Method 8270 may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

7.7.6 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are quantitated as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be summed and reported as the sum of both compounds.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Sec. 7.0 of Method 8000 and include calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8270:

8.2.1 The GC/MS system must be tuned to meet the DFTPP criteria listed in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the calibration verification acceptance criteria in Sec. 7.4, each 12 hours.

8.2.4 The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 7.6.1.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed, a septum is changed), see the guidance in Sec 8.2 of Method 8000 regarding whether recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations ranging from 5 to 1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7. These values are presented as guidance only and are not intended as absolute acceptance criteria. Laboratories should generate their own acceptance criteria for capillary column method performance. (See Method 8000.)

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 8.

9.3 Method performance data (using Method 3541 Automated Soxhlet extraction) are presented in Table 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 10 and were taken from Reference 7.

9.4 Surrogate precision and accuracy data are presented in Table 11 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by Method 8270.

9.5 Single laboratory precision and bias data (using Method 3545 Accelerated Solvent Extraction) for semivolatile organic compounds are presented in Table 12. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by Perstorp Environmental Soxtec™ (automated Soxhlet). The data presented in Table 12 represents seven replicate extractions and analyses for each individual sample and were taken from reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low-101.2%, mid-97.2% and high-99.2%.

9.6 Single laboratory precision and bias data (using Method 3561 SFE Extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (one, EC-1, a lake sediment from Environment Canada and the other, HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 13 and 14 and were taken from Reference 10.

9.7 Single laboratory precision and accuracy data (using Method 3561 SFE Extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO_2; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in Table 15 and were taken from Reference 11.

10.0 REFERENCES

1. Eichelberger, J.W., Harris, L.E., and Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems", Analytical Chemistry, 47, 995-1000, 1975.

2. "Method Detection Limit for Methods 624 and 625", Olynyk, P., Budde, W.L., and Eichelberger, J.W., unpublished report, October 1980.

3. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides", Final Report for EPA Contract 68-03-3102.

4. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects", Journal of the Association of Official Analytical Chemists (AOAC), 48, 1037, 1965.

5. Lucas, S.V., Kornfeld, R.A., "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes ", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

6. Engel, T.M., Kornfeld, R.A., Warner, J.S., and Andrews, K.D., "Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987, Contract 68-03-3224.

7. Lopez-Avila, V. (W. Beckert, Project Officer); "Development of a Soxtec Extraction Procedure for Extraction of Organic Compounds from Soils and Sediments"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV, October 1991; EPA 600/X-91/140.

8. Bursey, J., Merrill, R., McAllister, R., and McGaughey, J., "Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List", Vol. 1 and 2, U.S. Environmental Protection Agency, EPA 600/R-93/123a and b, (NTIS PB 93-227163 and 93-27171), Research Triangle Park, NC, July 1993.

9. Richter, B., Ezzell, J., and Felix, D., "Single Laboratory Method Validation Report: Extraction of Target Compound List/Priority Pollutant List BNAs and Pesticides using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD", Document 101124, Dionex Corporation, Salt Lake City, UT, June 16, 1994.

10. Lee, H.B., Peart, T.E., Hong-You, R.L., and Gere, D.R., "Supercritical Carbon Dioxide Extraction of Polycyclic Aromatic Hydrocarbons from Sediments", J. Chromatography, A 653 83-91 (1993).

11. Personal communication from Sue Warner, EPA Region 3, Central Regional Laboratory, 839 Bestgate Road, Annapolis, MD 21401.

TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	44,45,74
Thiophenol (Benzenethiol)	7.42	110	66,109,84
Methyl methanesulfonate	7.48	80	79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	79,95,109,140
Ethyl methanesulfonate	9.62	79	109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d_8 (IS)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	155,127,81,109
Diethyl sulfate	11.37	139	45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	108,77,79,90
Hexachloropropene	12.45	213	211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	41,42,68,69
Acetophenone	12.67	105	71,51,120
4-Methylphenol	12.82	107	108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	107,77,51,79
3-Methylphenol	12.93	107	108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,55,56,41
1,4-Phenylenediamine	13.62	108	80,53,54,52
1-Chloronaphthalene	13.65[a]	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	76,50,148
o-Anisidine	15.00	108	80,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d_{10} (IS)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	164,126,98,63
4-Chloroaniline	15.50	127	129,65,92
Isosafrole	15.60	162	131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	104,102,76,50,130
p-Cresidine	16.45	122	94,137,77,93
Dichlorovos	16.48	109	185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	135,134,91,77
N-Nitrosodi-n-butylamine	16.73	84	57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	104,77,103,135

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramide	17.33	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	214,179,108,143,218
1-Naphthylamine	18.20	143	115,89,63
1-Acetyl-2-thiourea	18.22	118	43,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,79,106,94
Thionazine	19.35	107	96,97,143,79,68
4-Nitroaniline	19.37	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	75,50,76,92,122
Mevinphos	19.90	127	192,109,67,164
Naled	20.03	109	145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	76,50,75,92,122
Diallate (cis or trans)	20.57	86	234,43,70
1,2-Dinitrobenzene	20.58	168	50,63,74
Diallate (trans or cis)	20.78	86	234,43,70
Pentachlorobenzene	21.35	250	252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	79,52,138,153,77
Pentachloronitrobenzene	21.72	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	131,230,166,234,168
Dihydrosaffrole	22.42	135	64,77
Demeton-O	22.72	88	89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	74,213,120,91,63
Dicrotophos	23.82	127	67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	43,264,41,290
Bromoxynil	23.90	277	279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	192,67,97,109
Phorate	24.10	75	121,97,93,260

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Sulfallate	24.23	188	88,72,60,44
Demeton-S	24.30	88	60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	93,125,143,229
Phenobarbital	24.70	204	117,232,146,161
Carbofuran	24.90	164	149,131,122
Octamethyl pyrophosphoramide	24.95	135	44,199,286,153,243
4-Aminobiphenyl	25.08	169	168,170,115
Dioxathion	25.25	97	125,270,153
Terbufos	25.35	231	57,97,153,103
α,α-Dimethylphenylamine	25.43	58	91,65,134,42
Pronamide	25.48	173	175,145,109,147
Aminoazobenzene	25.72	197	92,120,65,77
Dichlone	25.77	191	163,226,228,135,193
Dinoseb	25.83	211	163,147,117,240
Disulfoton	25.83	88	97,89,142,186
Fluchloralin	25.88	306	63,326,328,264,65
Mexacarbate	26.02	165	150,134,164,222
4,4'-Oxydianiline	26.08	200	108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	152,141,169,151
Phosphamidon	26.85	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	185,41,193,266
Methyl parathion	27.03	109	125,263,79,93
Carbaryl	27.17	144	115,116,201
Dimethylaminoazobenzene	27.50	225	120,77,105,148,42
Propylthiouracil	27.68	170	142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d_{12} (IS)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	125,127,93,158
Kepone	28.18	272	274,237,178,143,270
Fenthion	28.37	278	125,109,169,153
Parathion	28.40	109	97,291,139,155
Anilazine	28.47	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	106,196,180
Carbophenothion	28.58	157	97,121,342,159,199
5-Nitroacenaphthene	28.73	199	152,169,141,115
Methapyrilene	28.77	97	50,191,71
Isodrin	28.95	193	66,195,263,265,147

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Captan	29.47	79	149,77,119,117
Chlorfenvinphos	29.53	267	269,323,325,295
Crotoxyphos	29.73	127	105,193,166
Phosmet	30.03	160	77,93,317,76
EPN	30.11	157	169,185,141,323
Tetrachlorvinphos	30.27	329	109,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	167,195
Barban	30.83	222	51,87,224,257,153
Aramite	30.92	185	191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	139,253,111,141
Fensulfothion	31.87	293	97,308,125,292
Ethion	32.08	231	97,153,125,121
Diethylstilbestrol	32.15	268	145,107,239,121,159
Famphur	32.67	218	125,93,109,217
Tri-p-tolyl phosphate[b]	32.75	368	367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d_{12} (IS)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	241,239,120
5,5-Diphenylhydantoin	33.40	180	104,252,223,209
Captafol	33.47	79	77,80,107
Dinocap	33.47	69	41,39
Methoxychlor	33.55	227	228,152,114,274,212
2-Acetylaminofluorene	33.58	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	201,229
3-Methylcholanthrene	35.07	268	252,253,126,134,113
Phosalone	35.23	182	184,367,121,379
Azinphos-methyl	35.25	160	132,93,104,105
Leptophos	35.28	171	377,375,77,155,379
Mirex	35.43	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,119,217,219,199
Dibenz(a,j)acridine	36.40	279	280,277,250
Mestranol	36.48	277	310,174,147,242
Coumaphos	37.08	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	151,150,300

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	135,105,77
Hexachlorophene	47.98	196	198,209,211,406,408
Aldrin	--	66	263,220
Aroclor 1016	--	222	260,292
Aroclor 1221	--	190	224,260
Aroclor 1232	--	190	224,260
Aroclor 1242	--	222	256,292
Aroclor 1248	--	292	362,326
Aroclor 1254	--	292	362,326
Aroclor 1260	--	360	362,394
α-BHC	--	183	181,109
β-BHC	--	181	183,109
δ-BHC	--	183	181,109
γ-BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237,165
4,4'-DDE	--	246	248,176
4,4'-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
Endosulfan I	--	195	339,341
Endosulfan II	--	337	339,341
Endosulfan sulfate	--	272	387,422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr)	--	172	171
2-Fluorophenol (surr)	--	112	64
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d_5 (surr)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d_6 (surr)	--	99	42,71
Terphenyl-d_{14} (surr)	--	244	122,212
2,4,6-Tribromophenol (surr)	--	330	332,141
Toxaphene	--	159	231,233

IS = internal standard
surr = surrogate
[a]Estimated retention times
[b]Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
O,O,O-Triethyl phosphorothioate	NT	ND

[a] Sample EQLs are highly matrix-dependent. The EQLs listed here are provided for guidance and may not always be achievable.

[b] EQLs listed for soil/sediment are based on wet weight. Normally, data are reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. These EQLs are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined
NA = Not Applicable
NT = Not Tested

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c]EQL = (EQL for Low Soil/Sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a] Data taken from Reference 3.

[b] Alternate tuning criteria may be used, (e.g., CLP, Method 525, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 4

CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr)	1-Naphthylamine
N-Nitroso-di-n-propyl-amine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluor-anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluor-anthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl-phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	
Hexachlorobenzene	Pyrene	
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	
Pentachlorophenol	7,12-Dimethylbenz-(a)anthracene	
Pentachloronitrobenzene	Di-n-octyl phthalate	
Phenacetin	Indeno(1,2,3-cd) pyrene	
Phenanthrene	3-Methylchol-anthrene	
Pronamide		

(surr) = surrogate

TABLE 6

MULTILABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192

TABLE 6
(continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Aroclor 1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L

p, p_s = Measured percent recovery

D = Detected; result must be greater than zero

[a] Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{x}$-0.12	0.21$\bar{x}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{x}$-1.06	0.26$\bar{x}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{x}$-1.28	0.43$\bar{x}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{x}$-0.32	0.27$\bar{x}$-0.64
Benz(a)anthracene	0.88C-0.60	0.15$\bar{x}$+0.93	0.26$\bar{x}$-0.21
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{x}$+0.43	0.29$\bar{x}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{x}$+1.03	0.35$\bar{x}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{x}$+0.48	0.32$\bar{x}$+1.35
Benzo(g,h,i)perylene	0.98C-0.86	0.29$\bar{x}$+2.40	0.51$\bar{x}$-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
β-BHC	0.87C-0.94	0.20$\bar{x}$-0.58	0.30$\bar{x}$+1.94
δ-BHC	0.29C-1.09	0.34$\bar{x}$+0.86	0.93$\bar{x}$-0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35$\bar{x}$-0.99	0.35$\bar{x}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{x}$+1.34	0.26$\bar{x}$+2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24$\bar{x}$+0.28	0.25$\bar{x}$+1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26$\bar{x}$+0.73	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{x}$+0.66	0.16$\bar{x}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{x}$+0.52	0.13$\bar{x}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{x}$-0.94	0.30$\bar{x}$-0.46
Chrysene	0.93C-1.00	0.28$\bar{x}$+0.13	0.33$\bar{x}$-0.09
4,4'-DDD	0.56C-0.40	0.29$\bar{x}$-0.32	0.66$\bar{x}$-0.96
4,4'-DDE	0.70C-0.54	0.26$\bar{x}$-1.17	0.39$\bar{x}$-1.04
4,4'-DDT	0.79C-3.28	0.42$\bar{x}$+0.19	0.65$\bar{x}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{x}$+8.51	0.59$\bar{x}$+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{x}$+1.16	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{x}$+0.47	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{x}$+0.68	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{x}$+0.23	0.29$\bar{x}$+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28$\bar{x}$+7.33	0.47$\bar{x}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{x}$-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{x}$+1.44	0.52$\bar{x}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{x}$+0.19	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{x}$+1.06	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{x}$+1.26	0.19$\bar{x}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{x}$+1.19	0.37$\bar{x}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{x}$+2.47	0.63$\bar{x}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{x}$+3.91	0.73$\bar{x}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{x}$-0.73	0.28$\bar{x}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64

TABLE 7
(continued)

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{x}$+1.46	0.50$\bar{x}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{x}$+0.77	0.33$\bar{x}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{x}$-0.41	0.30$\bar{x}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{x}$+0.92	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{x}$+0.68	0.44$\bar{x}$+0.47
Aroclor 1260	0.81C-10.86	0.35$\bar{x}$+3.61	0.43$\bar{x}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{x}$+0.57	0.15$\bar{x}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{x}$+0.06	0.15$\bar{x}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{x}$+0.85	0.21$\bar{x}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{x}$+0.75	0.29$\bar{x}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{x}$+1.46	0.28$\bar{x}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{x}$+1.25	0.21$\bar{x}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{x}$+1.21	0.22$\bar{x}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{x}$+2.36	0.42$\bar{x}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{x}$+42.29	0.26$\bar{x}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{x}$+1.94	0.27$\bar{x}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{x}$+2.57	0.44$\bar{x}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{x}$+3.03	0.30$\bar{x}$+4.33
Phenol	0.43C+1.26	0.26$\bar{x}$+0.73	0.35$\bar{x}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{x}$+2.22	0.22$\bar{x}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

[a] Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 8

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

Compound	Percent Recovery on Day 0		Percent Recovery on Day 7	
	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 9

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANICS FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

Compound	Clay Soil		Topsoil	
	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 10

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9

TABLE 10
(continued)

Compound	Mean Recovery	RSD
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 11

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation Percent
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 11 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 12

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	**102.0**
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	**101.9**
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	**101.6**
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	**120.6**
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	**119.2**
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	**112.5**
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	**104.7**
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	**100.2**
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	**110.3**
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	**98.1**
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	**118.6**
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	**100.2**
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	**101.7**
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	**109.8**
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	**96.3**
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	**97.2**
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	**98.6**
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	**104.2**
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	**106.1**
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	**108.1**
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	**104.7**
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	**99.7**
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	**102.1**
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	**75.8**
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	**95.9**
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	**94.1**
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	**96.2**
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	**92.6**
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	**90.3**
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	**101.7**
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	**92.9**
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	**98.4**
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	**75.6**
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	**90.7**

TABLE 12 (cont.)

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	**98.8**
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	**94.4**
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	**95.4**
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	**99.1**
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	**96.8**
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	**95.8**
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	**93.7**
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	**81.2**
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	**100.6**
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	**101.2**
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	**99.1**
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	**102.7**
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	**105.2**
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	**116.5**
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	**101.5**
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	**102.9**
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	**99.0**
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	**103.1**
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	**99.9**
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	**102.7**
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	**98.6**
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	**66.4**
Average	**95.1**	**94.3**	**101.0**	**95.5**	**96.5**	**104.1**	**113.0**	**100.9**	**92.5**	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 15

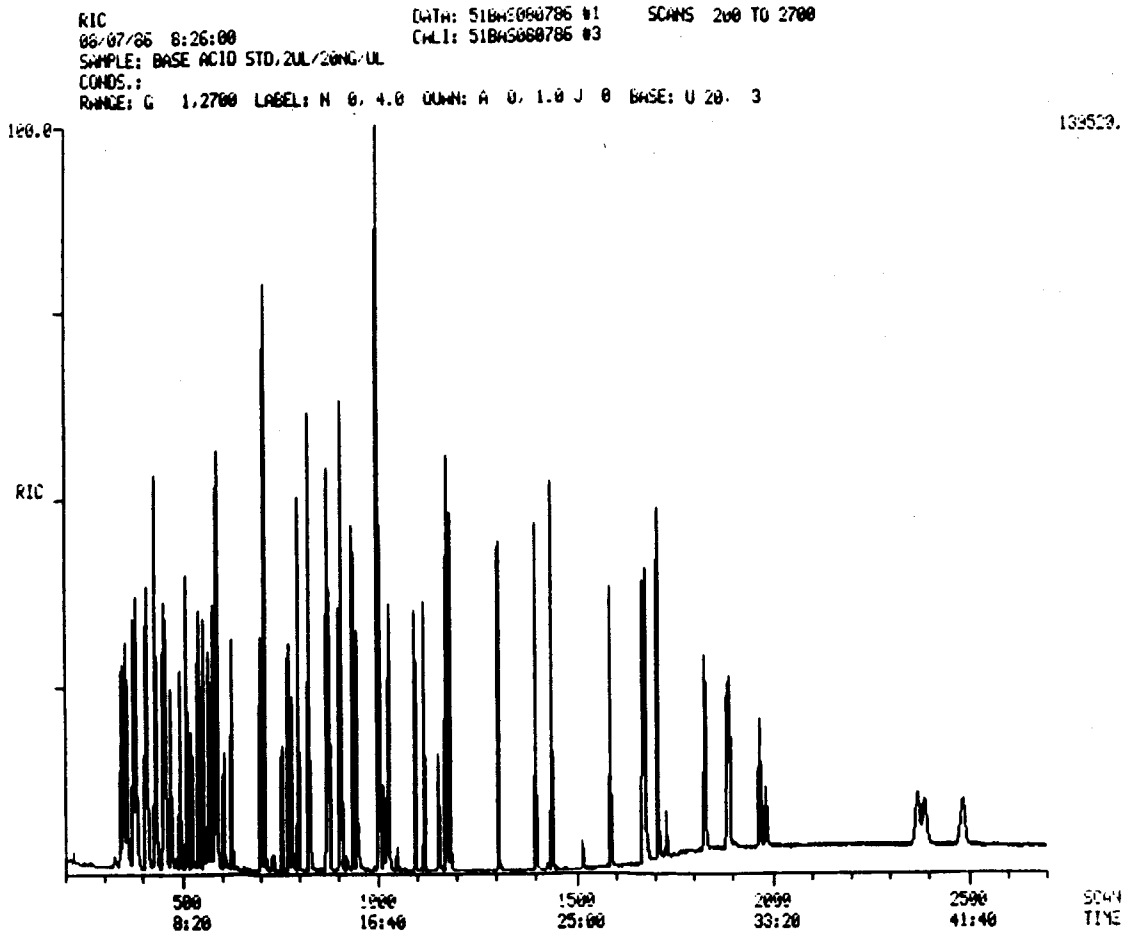
SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

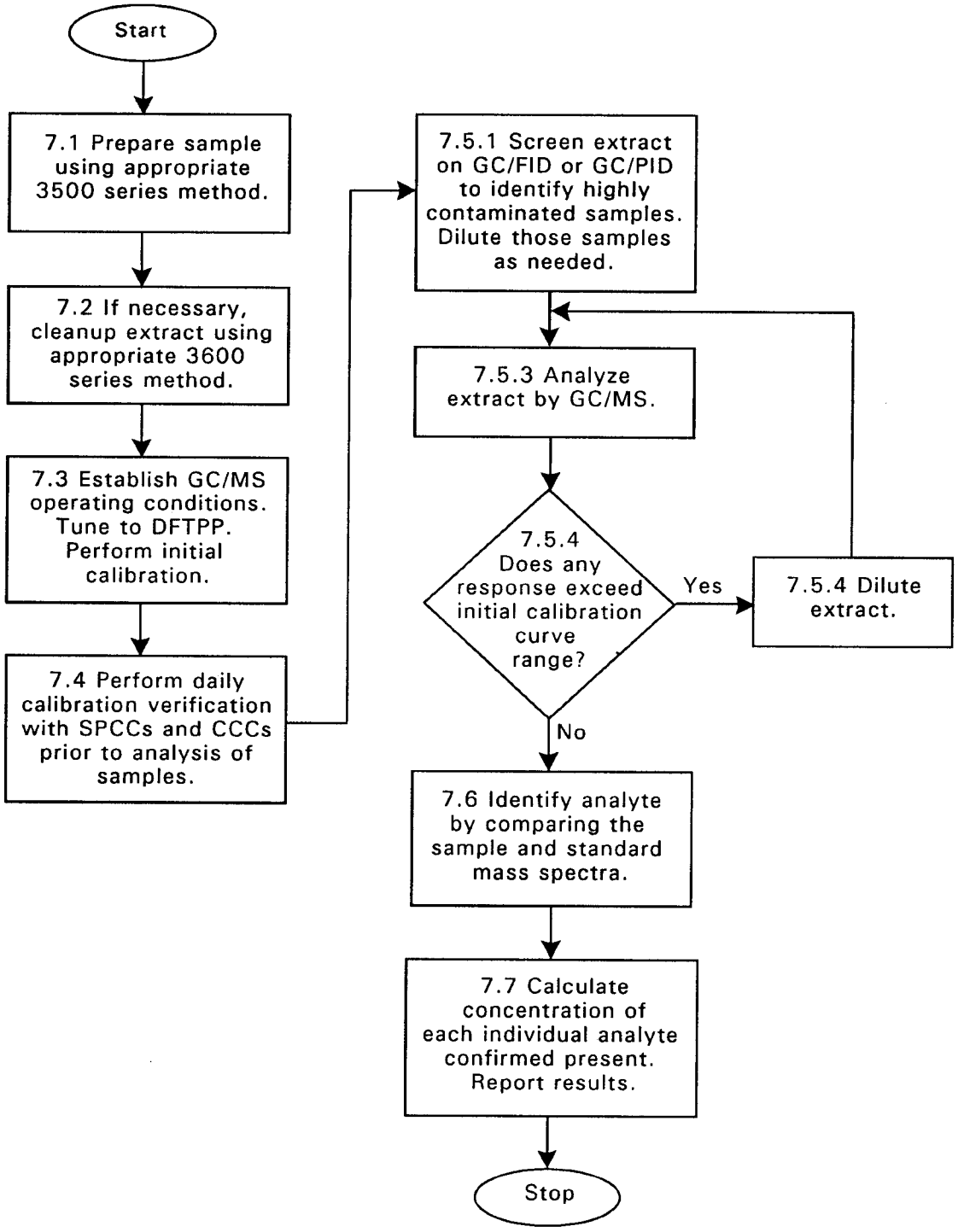
Compound	Certified Value (mg/kg)			SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4	±	8.2	29.55	91	10.5
2-Methylnaphthalene	62.1	±	11.5	76.13	122	2.0
Acenaphthene	632	±	105	577.28	91	2.9
Dibenzofuran	307	±	49	302.25	98	4.1
Fluorene	492	±	78	427.15	87	3.0
Phenanthrene	1618	±	340	1278.03	79	3.4
Anthracene	422	±	49	400.80	95	2.6
Fluoranthene	1280	±	220	1019.13	80	4.5
Pyrene	1033	±	285	911.82	88	3.1
Benz(a)anthracene	252	±	38	225.50	89	4.8
Chrysene	297	±	26	283.00	95	3.8
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153	±	22	130.88	86	10.7
Benzo(a)pyrene	97.2	±	17.1	58.28	60	6.5

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

FIGURE 1
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD




Start
7.1 Prepare sample using appropriate 3500 series method.
7.2 If necessary, cleanup extract using appropriate 3600 series method.
7.3 Establish GC/MS operating conditions. Tune to DFTPP. Perform initial calibration.
7.4 Perform daily calibration verification with SPCCs and CCCs prior to analysis of samples.
7.5.1 Screen extract on GC/FID or GC/PID to identify highly contaminated samples. Dilute those samples as needed.
7.5.3 Analyze extract by GC/MS.
7.5.4 Does any response exceed initial calibration curve range?
Yes
7.5.4 Dilute extract.
No
7.6 Identify analyte by comparing the sample and standard mass spectra.
7.7 Calculate concentration of each individual analyte confirmed present. Report results.
Stop

METHOD 3510C

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel.

2.2 The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Method 3510 is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520, and performing the initial extraction at the acid pH.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

4.8 pH indicator paper - pH range including the desired extraction pH.

4.9 Erlenmeyer flask - 250-mL.

4.10 Syringe - 5-mL.

4.11 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating to 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

5.6.1 Methylene chloride, CH_2Cl_2, boiling point 39°C.

5.6.2 Hexane, C_6H_{14}, boiling point 68.7°C.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$, boiling point 82.3°C.

5.6.4 Cyclohexane, C_6H_{12}, boiling point 80.7°C.

5.6.5 Acetonitrile, CH_3CN, boiling point 81.6°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sect. 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample. Alternatively, if the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used.

7.2 Pipet 1.0 mL of the surrogate spiking solution into each sample in the graduated cylinder (or sample bottle) and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and matrix spiking solution).

7.2.1 For the sample in each batch (see Chapter One) selected for use as a matrix spike sample, add 1.0 mL of the matrix spiking standard.

7.2.2 If Method 3640, Gel-Permeation Cleanup, is to be employed, add twice the volume of the surrogate spiking solution and the matrix spiking standard, since half of the extract is not recovered from the GPC apparatus. (Alternatively, use 1.0 mL of the spiking solutions and concentrate the final extract to half the normal volume, e.g., 0.5 mL instead of 1.0 mL).

7.3 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1, using 1:1 (v/v) sulfuric acid or 10 N sodium hydroxide. Lesser strengths of acid or base solution may be employed, provided that they do not result in a significant change (<1%) in the volume of sample extracted (see Secs. 5.3 and 5.5).

7.4 Quantitatively transfer the sample from the graduated cylinder (or sample bottle) to the separatory funnel. Use 60 mL of methylene chloride to rinse the cylinder (or bottle) and transfer this rinse solvent to the separatory funnel. If the sample was transferred directly from the sample bottle, refill the bottle to the mark made in Sec. 7.1 with water and then measure the volume of sample that was in the bottle.

7.5 Seal and shake the separatory funnel vigorously for 1 - 2 minutes with periodic venting to release excess pressure. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

7.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.7 Repeat the extraction two more times using fresh portions of solvent (Secs. 7.2 through 7.5). Combine the three solvent extracts.

7.8 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Secs. 7.2 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.9 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.10 Perform the concentration (if necessary) using the Kuderna-Danish Technique (Secs. 7.11.1 through 7.11.6).

7.11 K-D technique

7.11.1 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11.2 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.11.3 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.11.5 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4. Concentrate the extract, as described in Sec. 7.11.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11.6 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2) is used to adjust the extract to the final volume required.

7.12.1 Micro-Snyder column technique

If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or the exchange solvent, and adjust the final volume as indicated in Table 1, with solvent.

7.12.2 Nitrogen blowdown technique

7.12.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce contaminants.

7.12.2.2 The internal wall of the tube must be rinsed several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a PTFE-lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

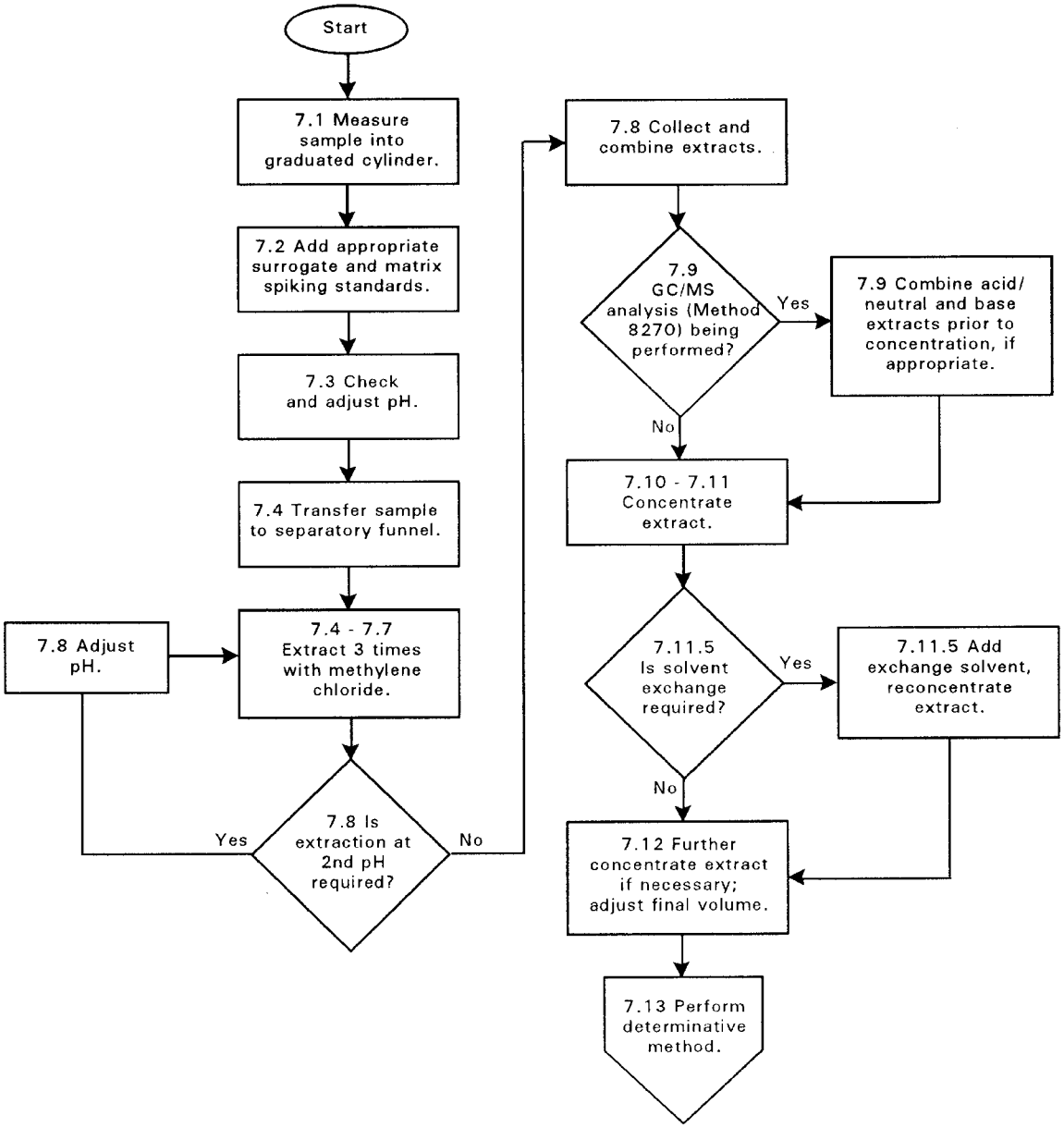
Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270[c,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

[d] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).


Start
7.1 Measure sample into graduated cylinder.
7.2 Add appropriate surrogate and matrix spiking standards.
7.3 Check and adjust pH.
7.4 Transfer sample to separatory funnel.
7.4 - 7.7 Extract 3 times with methylene chloride.
7.8 Adjust pH.
7.8 Is extraction at 2nd pH required?
Yes
No
7.8 Collect and combine extracts.
7.9 GC/MS analysis (Method 8270) being performed?
Yes
7.9 Combine acid/ neutral and base extracts prior to concentration, if appropriate.
No
7.10 - 7.11 Concentrate extract.
7.11.5 Is solvent exchange required?
Yes
7.11.5 Add exchange solvent, reconcentrate extract.
No
7.12 Further concentrate extract if necessary; adjust final volume.
7.13 Perform determinative method.

Appendix 28

SOP – Total P/$P0_4$ (EPA 365.2) (sediment analysis)

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD #: 365.2	Approved for NPDES (Issued 1971)
TITLE:	Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Single Reagent)
ANALYTE:	CAS # P Phosphorus 7723-14-0
INSTRUMENTATION:	Spectrophotometer
STORET No.	See Section 4

1.0 Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are defined in Section 4.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus are determined by calculation.

1.3 The methods are usable in the 0.01 to 0.5 mg P/L range.

2.0 Summary of Method

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion[(2)].

3.0 Sample Handling and Preservation

3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

3.3 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 mL conc. H_2SO_4 per liter and refrigeration at 4°C.

4.0 Definitions and Storet Numbers

4.1 Total Phosphorus (P)--all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)

4.1.1 Total Orthophosphate (P, ortho)--inorganic phosphorus [$(PO_4)^{-3}$] in the sample as measured by the direct colorimetric analysis procedure. (70507)

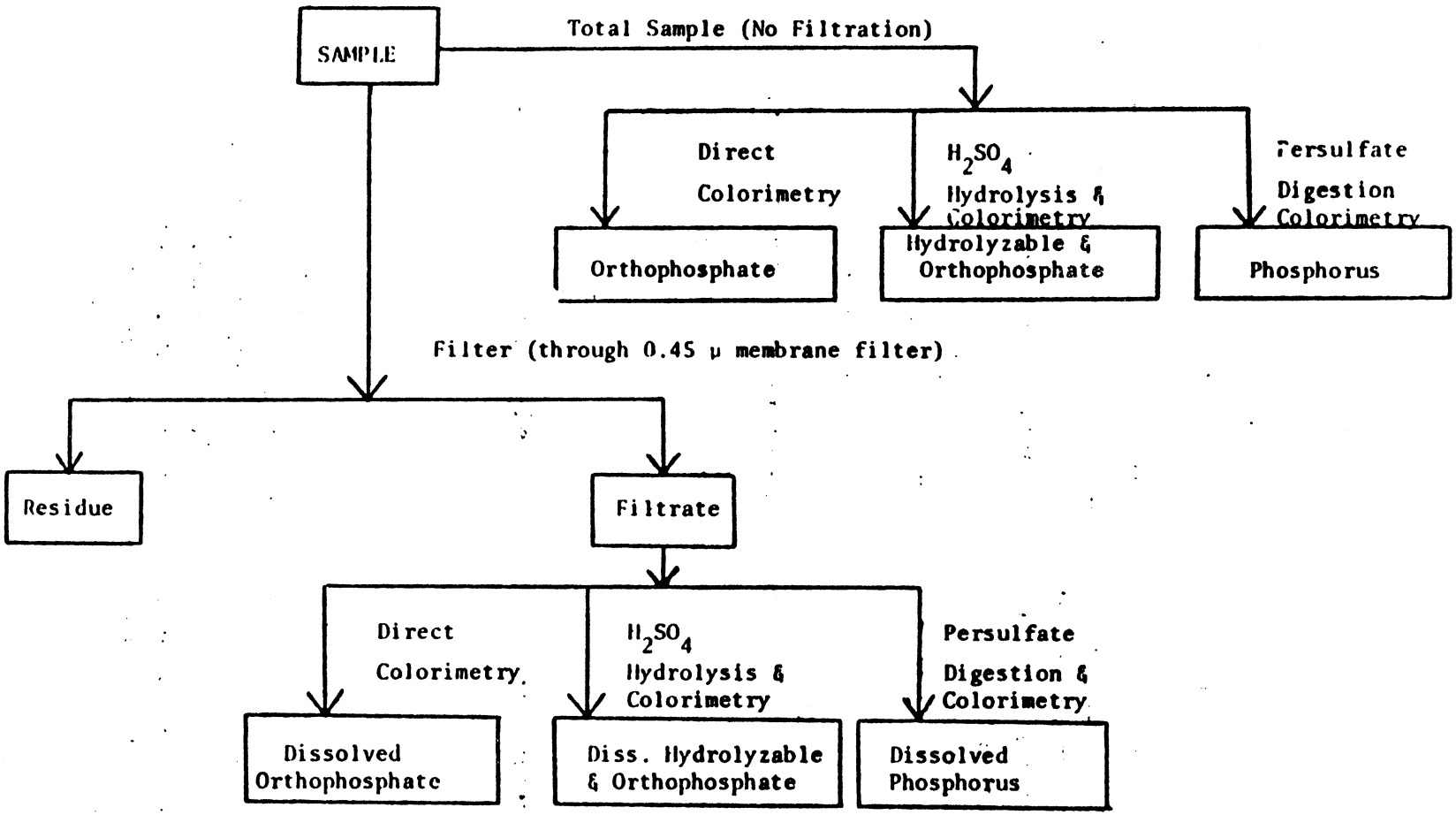


FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

4.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

4.1.3 Total Organic Phosphorus (P, org)--phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P-D)--all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P-D, ortho)--as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P-D, hydro)--as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P-D, org)--as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I) = (P)-(P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P-I, ortho)=(P, ortho)-(P-D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P-I, hydro)=(P, hydro)-(P-D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P-I, org)=(P, org) - (P-D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/L, to the third place.

5.0 Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

6.0 Apparatus

6.1 Photometer - A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled

with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7.0 Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 mL of conc H_2SO_4 with distilled water to 500 mL.

7.2 Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O \cdot 1/2H_2O$ dissolve in 400 mL distilled water in 500 mL volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_70_{24} \cdot 4H_2O$ in 500 mL of distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1 M: Dissolve 1.76 g of ascorbic acid in 100 mL of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 mL of the mixed reagent: 50 mL of 5N H_2SO_4, (7.1), 5 mL of antimony potassium tartrate solution (7.2), 15 mL of ammonium molybdate solution (7.3), and 30 mL of ascorbic acid solution (7.4). Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 mL conc. H_2SO_4 to 600 mL distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock phosphorus solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH2PO4, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 mL = 0.05 mg P.

7.9 Standard phosphorus solution: Dilute 10.0 mL of stock phosphorus solution (7.8) to 1000 mL with distilled water; 1.0 mL = 0.5 μg P.

7.9.1 Using standard solution, prepare the following standards in 50.0 mL volumetric flasks:

mL of Standard Phosphorus Solution (7.9)	Conc., mg/L
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

7.10 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 mL distilled water. Cool and dilute to 1 liter.

8.0 Procedure

8.1 Phosphorus

8.1.1 Add 1 mL of H_2SO_4 solution (7.6) to a 50 mL sample in a 125 mL Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30 10 minutes or until a final volume of about 10 mL is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Cool and dilute the sample to about 30 mL and adjust the pH of the sample to 7.0 ±0.2 with 1 N NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2-3 drops of acid (7.6) and filter. Dilute to 50 mL. Alternatively, if autoclaved see NOTE 1.

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 mL of H_2SO_4 solution (7.6) to a 50 mL sample in a 125 mL Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30 10 minutes or until a final volume of about 10 mL is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Cool and dilute the sample to about 30 mL and adjust the pH of the sample to 7.0 ±0.2 with NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2-3 drops of acid (7.6) and filter. Dilute to 50 mL. Alternatively, if autoclaved see NOTE 1.

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 The pH of the sample must be adjusted to 7 ± 0.2 using a pH meter.

8.3.2 Add 8.0 mL of combined reagent (7.5) to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 650 or 880 nm with a spectrophotometer, using the reagent blank as the reference solution. NOTE 1: If the same volume of sodium hydroxide solution is not used to adjust the pH of the standards and samples, a volume correction has to be employed.

9.0 Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/L. SEE NOTE 1.

10.0 Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias, mg P/liter
0.110	0.033	+3.09	+0.003
0.132	0.051	+11.99	+0.016
0.772	0.130	+2.96	+0.023
0.882	0.128	-0.92	-0.008

(FWPCA Method Study 2, Nutrient Analyses)

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias mg P/liter
0.029	0.010	-4.95	-0.001
0.038	0.008	-6.00	-0.002
0.335	0.018	-2.75	-0.009
0.383	0.023	-1.76	-0.007

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Murphy, J., and Riley, J., "A modified Single Solution for the Determination of Phosphate in Natural Waters", Anal. Chim. Acta., 27, 31(1962).
2. Gales, M., Jr., Julian, E., and Kroner, R., "Method for Quantitative Determination of Total Phosphorus in Water", Jour. AWWA, 58, No. 10, 1363 (1966).
3. Annual Book of ASTM Standards, Part 31, "Water", Standard D515-72, Method A, p 389 (1976).
4. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 476 and 481, (1975).

Appendix 29

SOP – NH_3/TKN (EPA 350.3/351.3) (sediment/water analysis)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD #: 350.3	Approved for NPDES (Issued 1974)
TITLE:	Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode)
ANALYTE:	CAS # Nitrogen, N 7727-37-9 CAS # Ammonia, NH_3 7664-41-7
INSTRUMENTATION:	ISE
STORET No.	Total 00610 Dissolved 00608

1.0 Scope and Application

1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
1.2 This method covers the range from 0.03 to 1400 mg NH_3-N/L. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.

2.0 Summary of Method

2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

3.0 Sample Handling and Preservation

3.1 Samples may be preserved with 2 mL of conc. H_2SO_4 per liter and stored at 4°C.

4.0 Interferences

4.1 Volatile amines act as a positive interference.
4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.

5.0 Apparatus

5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
5.2 Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.
5.3 Magnetic stirrer, thermally insulated, and Teflon-Coated stirring bar.

6.0 Reagents

6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 mL of distilled water. Cool and dilute to 1 liter with distilled water (6.1).

6.3 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg NH_3-N. Dissolve 3.819 g NH4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

6.4 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg NH_3-N. Dilute 10.0 mL of the stock solution (6. 3) to 1 liter with distilled water (6.1) in a volumetric flask.
NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350. 1).

7.0 Procedure

7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 mL of each standard solution in clean 150 mL beakers. Immerse electrode into standard of lowest concentration and add 1 mL of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.
NOTE 2: The pH of the solution after the addition of NaOH must be above 11. Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH3-N/L on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 mL of sample in 150 mL beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH_3-N/L.

8.0 Precision and Accuracy

8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH_3-N/L, standard deviations were ± 0.038, ± 0.017, ± 0.007, and ± 0.003, respectively.

8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg NH_3-N/L, recoveries were 96% and 91%, respectively.

Bibliography

1. Booth, R. L., and Thomas, R. F., "Selective Electrode Determination of Ammonia in Water and Wastes", Envir. Sci. Technology, 7, p 523-526 (1973).
2. Banwart, W. L., Bremner, J. M., and Tabatabai, M. A., "Determination of Ammonium in Soil Extracts and Water Samples by an Ammonia Electrode", Comm. Soil Sci. Plant.,3,p 449 (1952).
3. Midgley, D., and Torrance, K., "The Determination of Ammonia in Condensed Steam and Boiler Feed-Water with a Potentiometric Ammonia Probe", Analyst, 97 p 626-633 (1972).

METHOD #: 351.3	Approved for NPDES (Editorial Revision 1974, 1978)
TITLE:	Nitrogen, Kjeldahl, Total (Colorimetric; Titrimetric; Potentiometric)
ANALYTE:	CAS # N Nitrogen 7727-37-9
INSTRUMENTATION:	Spectrophotometer
STORET No.	00625

1.0 Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/L.

1.3 This method is described for macro and micro glassware systems.

2.0 Definitions

2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free- ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

3.0 Summary of Method

3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.

4.0 Sample Handling and Preservation

4.1 Samples may be preserved by addition of 2 mL of conc. H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic

nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

5.0 Interference

5.1 High nitrate concentrations (1OX or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

6.0 Apparatus

6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 mL flasks and suction takeoff to remove SO_3 fumes and water.

6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

7.0 Reagents

7.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.
NOTE 1: All solutions must be made with ammonia-free water.

7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 mL of 1:4 sulfuric acid (10.0 mL conc. H_2SO_4: 40 mL distilled water) and dilute to 100 mL with distilled water.

7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 mL distilled water and 400 mL conc. H_2SO_4. Add 50 mL mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.

7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_20_3 \bullet 5H_2O$ in distilled water and dilute to 1 liter.

7.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

7.6 Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in water and dilute to 1 liter with distilled water.

7.7 Sulfuric acid, standard solution: (0.02 N) 1 mL = 0.28 mg NH_3-N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 mL of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 mL of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

NOTE 2: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can the be prepared.

7.8 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg NH_3-N. Dissolve 3.819 g NH_4Cl in water and make up to 1 liter in a volumetric flask with distilled water.

7.9 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg NH_3-N. Dilute 10.0 mL of the stock solution (7. 8) with distilled water to 1 liter in a volumetric flask.

7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 mL of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

NOTE 3: Reagents 7.7, 7.8, 7.9, and 7.10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric-Distillation Procedure, Method 350.2).

8.0 Procedure

8.1 The distillation apparatus should be pre steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

8.2 Macro Kjeldahl system

8.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 mL Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/L	Sample Size mL
0-5	500
5-10	250
10-20	100
20-50	50.0
50-500	25.0

Dilute the sample, if required, to 500 mL with distilled water, and add 100 mL sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 mL distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 mL of sodium hydroxide - thiosulfate solution (7.4) without mixing.

NOTE 5: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the

aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 mL at the rate of 6-10 ml/min., into 50 mL of 2% boric acid (7.6) contained in a 500 mL Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 mL in the flask. These flasks should be marked at the 350 and the 500 mL volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 1 mg/L, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/L.

8.3 Micro Kjeldahl system

8.3.1 Place 50.0 mL of sample or an aliquot diluted to 50 mL in a 100 mL Kjeldahl flask and add 10 mL sulfuric acid-mercuric sulfate- potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 mL distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 mL of sodium hydroxide thiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 mL short-form Nessler tube.

8.3.4 Steam distill 30 mL at the rate of 6-10 ml/min., into 5 mL of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 mL. For concentrations above 1 mg/L the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/L.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 (7.7), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

mL of Standard 1.0 mL = 0.01 mg NH_3-N	mg NH_3-N / 50.0 mL
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 mL with ammonia free water, add 1 mL of Nessler Reagent (7.10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg NH_3-N for the standard curve. Develop color in the 50 mL diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Potentiometric, Ion Selective Electrode Method,(350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled, and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9.0 Calculation

9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/L, in the original sample as follows:

$$\text{TKN, } mg/L = \frac{(A - B)N \times F \times 1{,}000}{S}$$

where:

A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.
B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weigh to nitrogen (14mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, } mg/L = \frac{(A - B) \times 280}{S}$$

9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/L, in the original sample as follows:

$$\text{TKN, } mg/L = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3-N read from curve.
B = mL total distillate collected including the H_3BO_3.
C = mL distillate taken for Nesslerization.
D = mL of original sample taken.

9.3 Calculate Organic Kjeldahl Nitrogen in mg/L, as follows: Organic Kjeldahl Nitrogen = TKN--(NH_3-N.)

9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/L, in the original sample as follows:

$$\text{TKN, } mg/L = \frac{B}{D} \times A$$

where:

A = mg NH_3-N/L from electrode method standard curve.
B = volume of diluted distillate in mL.
D = mL of original sample taken.

10.0 Precision

10.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias mg N/liter
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	- 1.67	-0.08

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).
2. Schlueter, Albert, "Nitrate Interference In Total Kjeldahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7-77-017.

Appendix 30

SOP – Turbidity (USEPA 180.1) (water analysis)

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD 180.1

DETERMINATION OF TURBIDITY BY NEPHELOMETRY

Edited by James W. O'Dell
Inorganic Chemistry Branch
Chemistry Research Division

Revision 2.0
August 1993

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 180.1

DETERMINATION OF TURBIDITY BY NEPHELOMETRY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of turbidity in drinking, ground, surface, and saline waters, domestic and industrial wastes.

1.2 The applicable range is 0-40 nephelometric turbidity units (NTU). Higher values may be obtained with dilution of the sample.

2.0 SUMMARY OF METHOD

2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer designed according to specifications given in Sections 6.1 and 6.2. A primary standard suspension is used to calibrate the instrument. A secondary standard suspension is used as a daily calibration check and is monitored periodically for deterioration using one of the primary standards.

2.1.1 Formazin polymer is used as a primary turbidity suspension for water because it is more reproducible than other types of standards previously used for turbidity analysis.

2.1.2 A commercially available polymer primary standard is also approved for use for the National Interim Primary Drinking Water Regulations. This standard is identified as AMCO-AEPA-1, available from Advanced Polymer Systems.

3.0 DEFINITIONS

3.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogates analytes.

3.2 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.3 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method

analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.5 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.6 **Primary Calibration Standard (PCAL)** -- A suspension prepared from the primary dilution stock standard suspension. The PCAL suspensions are used to calibrate the instrument response with respect to analyte concentration.

3.7 **Quality Control Sample (QCS)** -- A solution of the method analyte of known concentrations that is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance.

3.8 **Secondary Calibration Standards (SCAL)** -- Commercially prepared, stabilized sealed liquid or gel turbidity standards calibrated against properly prepared and diluted formazin or styrene divinylbenzene polymers.

3.9 **Stock Standard Suspension (SSS)** -- A concentrated suspension containing the analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source. Stock standard suspension is used to prepare calibration suspensions and other needed suspensions.

4.0 INTERFERENCES

4.1 The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles can cause high readings.

4.2 The presence of true color, that is the color of water which is due to dissolved substances that absorb light, will cause turbidities to be low, although this effect is generally not significant with drinking waters.

4.3 Light absorbing materials such as activated carbon in significant concentrations can cause low readings.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in

this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 Hydrazine Sulfate (Section 7.2.1) is a carcinogen. It is highly toxic and may be fatal if inhaled, swallowed, or absorbed through the skin. Formazin can contain residual hydrazine sulfate. Proper protection should be employed.

6.0 EQUIPMENT AND SUPPLIES

6.1 The turbidimeter shall consist of a nephelometer, with light source for illuminating the sample, and one or more photo-electric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be designed so that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.

6.2 Differences in physical design of turbidimeters will cause differences in measured values for turbidity, even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

6.2.1 Light source: Tungsten lamp operated at a color temperature between 2200-3000°K.

6.2.2 Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

6.2.3 Detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°. The detector, and filter system if used, shall have a spectral peak response between 400 nm and 600 nm.

6.3 The sensitivity of the instrument should permit detection of a turbidity difference of 0.02 NTU or less in waters having turbidities less than 1 unit. The instrument should measure from 0-40 units turbidity. Several ranges may be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

6.4 The sample tubes to be used with the available instrument must be of clear, colorless glass or plastic. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. A light coating of silicon oil may be used to mask minor imperfections in glass tubes. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled. Tubes should be checked, indexed and read at the orientation that produces the lowest background blank value.

6.5 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.6 Glassware -- Class A volumetric flasks and pipets as required.

7.0 REAGENTS AND STANDARDS

7.1 Reagent water, turbidity-free: Pass deionized distilled water through a 0.45µ pore size membrane filter, if such filtered water shows a lower turbidity than unfiltered distilled water.

7.2 Stock standard suspension (Formazin):

7.2.1 Dissolve 1.00 g hydrazine sulfate, $(NH_2)_2.H_2SO_4$ (CASRN 10034-93-2) in reagent water and dilute to 100 mL in a volumetric flask. **CAUTION**-- carcinogen.

7.2.2 Dissolve 10.00 g hexamethylenetetramine (CASRN 100-97-0) in reagent water and dilute to 100 mL in a volumetric flask. In a 100 mL volumetric flask, mix 5.0 mL of each solution (Sections 7.2.1 and 7.2.2). Allow to stand 24 hours at 25 ±3°C, then dilute to the mark with reagent water.

7.3 Primary calibration standards: Mix and dilute 10.00 mL of stock standard suspension (Section 7.2) to 100 mL with reagent water. The turbidity of this suspension is defined as 40 NTU. For other values, mix and dilute portions of this suspension as required.

7.3.1 A new stock standard suspension (Section 7.2) should be prepared each month. Primary calibration standards (Section 7.3) should be prepared daily by dilution of the stock standard suspension.

7.4 Formazin in commercially prepared primary concentrated stock standard suspension (SSS) may be diluted and used as required. Dilute turbidity standards should be prepared daily.

7.5 AMCO-AEPA-1 Styrene Divinylbenzene polymer primary standards are available for specific instruments and require no preparation or dilution prior to use.

7.6 Secondary standards may be acceptable as a daily calibration check, but must be monitored on a routine basis for deterioration and replaced as required.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with turbidity free water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

8.2 No chemical preservation is required. Cool sample to 4°C.

8.3 Samples should be analyzed as soon as possible after collection. If storage is required, samples maintained at 4°C may be held for up to 48 hours.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and analysis of laboratory reagent blanks and other solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE.

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS).

9.2.2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analysis of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before continuing with on-going analyses.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment.

9.3.2 Instrument Performance Check Solution (IPC) -- For all determinations, the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is

within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data. NOTE: Secondary calibration standards (SS) may also be used as the IPC.

9.3.3 Where additional reference materials such as Performance Evaluation samples are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Solid standards, such as those made of lucite blocks, should never be used due to potential calibration changes caused by surface scratches. If a pre-calibrated scale is not supplied, calibration curves should be prepared for each range of the instrument.

11.0 PROCEDURE

11.1 Turbidities less than 40 units: If possible, allow samples to come to room temperature before analysis. Mix the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

11.2 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

11.2.1 Some turbidimeters are equipped with several separate scales. The higher scales are to be used only as indicators of required dilution volumes to reduce readings to less than 40 NTU.

Note: Comparative work performed in the Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) indicates a progressive error on sample turbidities in excess of 40 units.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Multiply sample readings by appropriate dilution to obtain final reading.

12.2 Report results as follows:

NTU	Record to Nearest:
0.0 - 1.0	0.05
1 - 10	0.1
10 - 40	1
40 - 100	5
100 - 400	10
400 - 1000	50
>1000	100

13.0 METHOD PERFORMANCE

13.1 In a single laboratory (EMSL-Cincinnati), using surface water samples at levels of 26, 41, 75, and 180 NTU, the standard deviations were ±0.60, ±0.94, ±1.2, and ±4.7 units, respectively.

13.2 The interlaboratory precision and accuracy data in Table 1 were developed using a reagent water matrix. Values are in NTU.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American

Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

15.1 The U.S. Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Section 14.3.

16.0 REFERENCES

1. Annual Book of ASTM Standards, Volume 11.01 Water (1), Standard D1889-88A, p. 359, (1993).

2. Standard Methods for the Examination of Water and Wastewater, 18th Edition, pp. 2-9, Method 2130B, (1992).

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. INTERLABORATORY PRECISION AND ACCURACY DATA

Number of Values Reported	True Value (T)	Mean (X)	Residual for X	Standard Deviation (S)	Residual for S
373	0.450	0.4864	0.0027	0.1071	-0.0078
374	0.600	0.6026	-0.0244	0.1048	-0.0211
289	0.65	0.6931	0.0183	0.1301	0.0005
482	0.910	0.9244	0.0013	0.2512	0.1024
484	0.910	0.9919	0.0688	0.1486	-0.0002
489	1.00	0.9405	-0.0686	0.1318	-0.0236
640	1.36	1.3456	-0.0074	0.1894	0.0075
487	3.40	3.2616	-0.0401	0.3219	-0.0103
288	4.8	4.5684	-0.0706	0.3776	-0.0577
714	5.60	5.6984	0.2952	0.4411	-0.0531
641	5.95	5.6026	-0.1350	0.4122	-0.1078

REGRESSIONS: $X = 0.955T + 0.54$, $S = 0.074T + 0.082$

Appendix 31

SOP – COD (USEPA 410.4)

BLASLAND, BOUCK & LEE, INC.
engineers & scientists

METHOD 410.4

THE DETERMINATION OF CHEMICAL OXYGEN DEMAND BY SEMI-AUTOMATED COLORIMETRY

Edited by James W. O'Dell
Inorganic Chemistry Branch
Chemistry Research Division

Revision 2.0
August 1993

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268
METHOD 410.4

THE DETERMINATION OF CHEMICAL OXYGEN DEMAND BY SEMI-AUTOMATED COLORIMETRY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of chemical oxygen demand (COD) in ground and surface waters, domestic and industrial wastes.

1.2 The applicable range is 3-900 mg/L.

2.0 SUMMARY OF METHOD

2.1 Sample, blanks, and standards in sealed tubes are heated in an oven or block digestor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digester, cooled, and measured spectrophotometrically at 600 nm. The colorimetric determination may also be performed manually.

2.2 Reduced volume versions of this method that use the same reagents and molar ratios are acceptable provided they meet the quality control and performance requirements stated in the method.

2.3 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Section 9.0, Quality Control.

3.0 DEFINITIONS

3.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.4 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5 **Laboratory Fortified Sample Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.8 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.9 **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.10 **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.11 **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.0 INTERFERENCES

4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Mercuric sulfate (Section 7.2)

5.3.2 Potassium dichromate (Section 7.2)

5.3.3 Sulfuric acid (Sections 7.2, 7.3, and 7.4)

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware -- Class A volumetric flasks and pipets as required.

6.3 Block digestor or drying oven capable of maintaining 150°C.

6.4 Muffle furnace capable of 500°C.

6.5 Culture tube with Teflon-lined screw cap, 16 x 100 mm or 25 x 150 mm.

6.6 Automated continuous flow analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.6.1 Sampling device (sampler)

6.6.2 Multichannel pump

6.6.3 Reaction unit or manifold

6.6.4 Colorimetric detector

6.6.5 Data recording device

7.0 REAGENTS AND STANDARDS

7.1 Reagent water: Distilled or deionized water, free of the analyte of interest. ASTM Type II or equivalent.

7.2 Digestion solution: Add 5.1 g potassium dichromate $K_2Cr_2O_7$ (CASRN 7778-50-9), 84 mL conc. sulfuric acid H_2SO_4 (CASRN 8014-95-7) and 16.7 g mercuric sulfate $HgSO_4$ (CASRN 7783-35-9) to 250 mL of reagent water, cool and dilute to 500 mL. CAUTION: CAN BE VERY HOT!

7.3 Catalyst solution: Add 22 g silver sulfate Ag_2SO_4 (CASRN 10294-26-5) to a 4.09 kg bottle of conc. H_2SO_4. Stir until dissolved.

7.4 Sampler wash solution: Add 250 mL of conc. H_2SO_4 to 250 mL of reagent water. CAUTION: PREPARE CAREFULLY, HIGH HEAT GENERATION!

7.5 Stock potassium hydrogen phthalate standard: Dissolve 0.425 g KHP (CASRN 877-24-7) in 400 mL of reagent water and dilute to 500 mL. 1 mL = 1 mg COD.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleansed and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

8.2 Samples must be preserved with H_2SO_4 to a pH <2 and cooled to 4°C at the time of collection.

8.3 Samples should be analyzed as soon as possible after collection. If storage is required, preserved samples maintained at 4°C may be held for up to 28 days.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[2] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

MDLs should be determined every six months, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = x + 3S$$
$$\text{LOWER CONTROL LIMIT} = x - 3S$$

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to established an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument Performance Check Solution (IPC) -- For all determinations, the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required), and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case, the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample

9.4.3 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.4 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of at least three standards, covering the desired range, by diluting appropriate volumes of the stock standard (Section 7.5)and a blank.

10.2 Process standards and blanks as described under Procedure (Section 11.0).

10.3 Set up manifold as shown in Figure 1.

10.4 Allow the instrument to warm up as required. Pump all reagents until a stable baseline is achieved.

10.5 Place appropriate standards in the sampler in order of decreasing concentration and perform analysis.

10.6 Prepare a standard curve by plotting instrument response against concentration values. A calibration curve may be fitted to the calibration solutions concentration / response data using computer or calculator based regression curve fitting techniques. Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration.

10.7 After the calibration has been established, it must be verified by the analysis of a suitable QCS. If measurements exceed ±10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis. Periodic reanalysis of the QCS is recommended as a continuing calibration check.

11.0 PROCEDURE

11.1 Wash all culture tubes and screw caps with 20% H_2SO_4 before their first use to prevent contamination. Trace contamination may be removed from the tubes by igniting them in a muffle furnace at 500°C for one hour.

11.2 Pipet 2.5 mL of sample, standard or blank, into 16 x 100 mm tubes or 10 mL into 25 x 100 mm tubes.

11.3 Add 1.5 mL of digestion solution (Section 7.2) to the 16 x 100 mm tubes or 6.0 mL to the 25 x 150 mm tubes and mix.

11.4 Add 3.5 mL of catalyst solution (Section 7.3) carefully down the side of the 16 x 100 mm tubes or 14.0 mL to the 25 x 150 mm tubes.

11.5 Cap tubes tightly and shake to mix layer. **CAUTION:** Tubes are hot.

11.6 Place tubes into a block digester or oven at 150°C and heat for two hours.

11.7 Remove, mix, and cool tubes. Allow any precipitate to settle.

11.8 Fill and connect reagent containers and start system. Allow the instrument to warm up as required. Pump all reagents until a stable baseline is achieved.

11.9 Place standards, blanks, and samples in sampler tray. Calibrate instrument, and begin analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

l2.3 Report results in mg/L.

13.0 METHOD PERFORMANCE

13.1 The interlaboratory precision and accuracy data in Table 1 were developed using a reagent water matrix. Values are in mg COD/L.

13.2 Single laboratory precision data can be estimated at 50-75% of the interlaboratory precision estimates.

l4.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and

spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Section 14.3.

16.0 REFERENCES

1. Jirka, A.M., and M.J. Carter, "Micro-Semi-Automated Analysis of Surface and .Wastewaters for Chemical Oxygen Demand". Anal. Chem. 47:1397, (1975).

2. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. INTERLABORATORY PRECISION AND ACCURACY DATA

Number of Values Reported	True Value (T)	Mean (X)	Residual for X	Standard Deviation (S)	Residual for S
241	18.2	18.9398	-0.4220	5.2026	-0.0964
144	26.3	26.1454	-1.0445	5.6142	-0.0888
140	28.5	32.7275	3.4115	6.2230	0.4103
112	43.5	42.8360	-0.9763	6.4351	-0.1257
261	46.6	45.3034	-1.5049	6.7677	0.0523
181	50.0	49.4740	-0.6201	7.0494	0.1644
262	65.4	63.2876	-1.6894	7.6041	-0.0489
182	76.2	75.7960	0.3816	8.4490	0.2573
141	91.7	94.0772	3.6833	7.9289	-1.0358
250	121	117.7424	-0.9678	9.6197	-0.8063
144	201	196.9391	0.9151	14.6995	0.2837
113	229	221.8109	-1.2730	17.3403	1.5280

REGRESSIONS: $X = 0.966T - 1.773$, $S = 0.050T + 4.391$

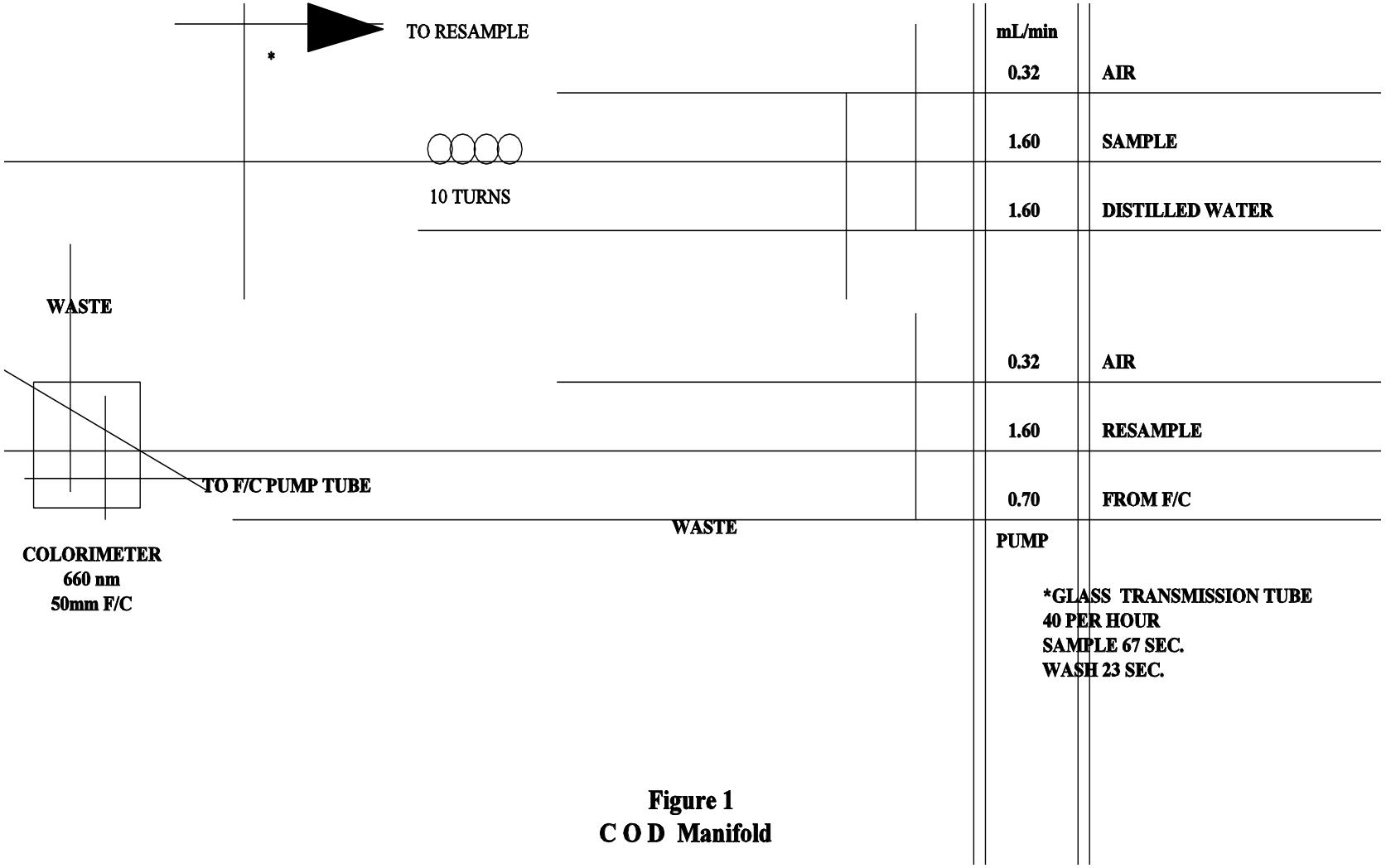


Figure 1
C O D Manifold