70005

PHASE 2B
SAMPLING AND ANALYSIS/QUALITY ASSURANCE PROJECT PLAN

VOLUME 2
BENTHIC INVERTEBRATE AND SEDIMENT GRAB SAMPLING

HUDSON RIVER PCB REASSESSMENT RI/FS

USEPA WORK ASSIGNMENT NO. 013-2N84

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Alternative Remedial Contracting Strategy (ARCS)

for

Hazardous Waste Remedial Services

Prepared by

TAMS CONSULTANTS, INC.
and
GRADIENT CORPORATION

Hudson River PCB Reassessment RI/FS
Phase 2B SAP/QAPjP - Volume 2
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Table of Contents

Table of Contents (cont.)

Table of Contents (cont.)

LIST OF TABLES

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LIST OF FIGURES

APPENDICES

Note: In order to maintain consistency among various Phase 2B project plans, the numbering of Appendices is uniform throughout the various plans. Therefore, Appendices which are not relevant to this SAP/QAPjP are omitted and are designated below as "Not Applicable".

and monitoring is on-going. The Waterford Treatment Plant treatability study concluded that the water supplied for drinking water meets Federal and State PCB standards.

In 1989, USEPA announced that the No Action alternative for Upper Hudson river sediments would be reassessed, and in 1990 issued a Scope of Work outlining a three phased reassessment:

Phase 1	•	Preliminary Reassessment or Interim Site Characterization and Evaluations
Phase 2	•	Further Sampling and Analysis
Phase 3	•	Feasibility Study

The Phase 1 Report-Review Copy was issued in August 1991. In order to complete the entire investigation in a timely manner, an initial sampling program, called Phase 2A, was proposed and implemented by USEPA in November, 1991. A Phase 2A Sampling Plan-Review Copy was issued in September, 1991 outlining the sampling tasks for Phase 2A. The complete Phase 2 Work Plan was issued in September, 1992. This Phase 2B (Volume 2) SAP/QAPjP covers the second of five investigation tasks to be conducted under Phase 2B.

3.2 Benthic Invertebrate and Sediment Sampling Objectives

Two major sampling efforts are proposed to provide site specific data for the ecological assessment. These efforts and their objectives are:

- **The Thompson Island Pool Area Benthic Invertebrate and Sediment Sampling (Upper Hudson River)** - To quantitatively describe benthic invertebrate (i.e., those organisms attached to, living on, in or near the river bed) communities in areas of significantly different PCB concentrations within the Thompson Island Pool (River Mile [RM] 188.5-194). Sample analyses will include congener-specific PCB analysis on benthic invertebrates, associated sediments and other parameters potentially affecting benthic community structure. Five areas, including one station used as a background or control area, will be selected to reflect different PCB sediment

concentrations. A station in the vicinity of the mouth of Snook Kill (RM 191.5) will serve as the control or background area. If Snook Kill is found to be an inappropriate control during PCB field-screening procedures (i.e., if field screening indicates the presence of a detectable concentration of PCBs), the control station will be moved to another location. The other four areas will be located at approximately RM 194, 192, 190, and 189. The precise sampling areas will be selected based on criteria described in Section 6. The sampling stations will be designated in order to examine the potential effects of PCBs on benthic invertebrate community structure and bioaccumulation.

In addition, one sample of epibenthic invertebrates (organisms that live on the river bottom) will be collected at each sampling station; the sample will be analyzed for PCB congeners, lipid content, and biomass. These samples will assist in quantifying PCB concentrations in epibenthic invertebrates and estimating the PCB concentrations in organisms that feed on them (i.e., fish).

- **The Upper and Lower Hudson River Sediment and Benthic Invertebrate Sampling** - The primary focus of this study will be to examine the PCB concentrations in sediments along the Hudson River in ecologically significant areas (many of the sampling stations are designated as significant coastal fish and wildlife habitats by NYSDEC) to estimate the potential adverse ecological effects from exposure to present levels of PCBs. The proposed sampling stations are located at RM 210, 203, 196.8, 175, 158, 142, 135, 123, 118, 100, 88, 58, 40 and 24. Benthic invertebrates, including one epibenthic sample per station, will be analyzed for PCBs at the four federally designated Hudson River Estuarine Sanctuaries (RM 123, 100, 40 and 24) and one additional location (RM 88). The benthic invertebrate sampling will represent a "worst case" exposure scenario (highest potential exposure) in environmentally sensitive areas.

A qualitative evaluation of each sampling station will be made by an experienced biologist(s) at time of sampling for both studies. The evaluations will assist in characterizing the habitat at each station and interpreting the results of each study.

Data objectives and required analyses for each study differ according to specific ecological objectives and media examined. In the following section of this SAP/QAPjP, the specific objectives of each study are

discussed along with the justification for individual analyses. Locations of the proposed benthic invertebrate and sediment sampling stations in the Upper and Lower Hudson are shown in Figures 3-1 and 3-2, respectively.

3.2.1 Thompson Island Pool Area - Benthic Invertebrate and Sediment Sampling Study

The Thompson Island Pool area was chosen as the focus of this study because previous investigations indicated that it was a highly contaminated area. Therefore, adverse ecological effects are more likely to be detected here, than in areas with lower PCB concentrations.

The Thompson Island Pool Study has six quantitative components in addition to the qualitative field evaluation. These components are: 1) determining the total biomass of benthic invertebrate samples at each station; 2) quantifying the species diversity and abundance of benthic invertebrate communities at each sampling station; 3) analyzing benthic invertebrates for congener-specific PCBs; 4) determining the lipid content of benthic invertebrates; 5) quantifying water quality parameters (e.g., temperature, pH) to determine if differences exist between stations; and 6) quantifying sediment properties at each station, including PCB analysis on a congener-specific level. Each of these six components are described below.

3.2.1.1 Biomass of Benthic Invertebrates

The total benthic biomass (wet weight) of each sample will be determined prior to sorting. After sorting, up to three major taxonomic group will be weighed in order to establish relative contributions to the total biomass. One sample of epibenthic invertebrates will be collected at each sampling station later and weighed to determine the biomass.

3.2.1.2 Species Diversity and Abundance

Species diversity and abundance can serve as an indicator of the general health of a biological community. Therefore, benthic macroinvertebrates (i.e., organisms that are retained on a 0.5 mm mesh) will be sorted and identified to the lowest practical taxonomic level. The number of individuals of each taxonomic group will be recorded and expressed in terms of relative abundance.

3.2.1.3 Congener-Specific PCB Analysis of Benthic Invertebrates

A sample comprised of all the individuals collected (i.e., total biomass) will be analyzed for congener-specific PCBs. This will assist in determining the extent of PCB bioaccumulation in benthic invertebrates, if any, and if certain congeners are preferentially taken up by benthic invertebrates. If enough individuals of a discrete taxon are present to provide an adequate sample quantity for PCB analysis ($\geq$ 1 gram), separate PCB analyses will be performed for each major taxon, to a maximum of one total biomass sample and three individual taxon samples. If enough organisms are available, the life stages of each major taxon will be analyzed separately.

In addition, one sample of epibenthic invertebrates will be collected at each sampling station and analyzed for congener-specific PCBs. These samples will assist in quantifying PCB concentrations in epibenthic invertebrates.

3.2.1.4 Lipid Content of Benthic Invertebrates

PCBs are lipophilic compounds, and therefore the average lipid content of an organism can affect its bioaccumulation potential. Lipid content will be determined on a sample consisting of all individuals collected. If enough individuals of a discrete taxon are present, separate lipid analyses will be performed for each major taxon, to a maximum of one total biomass sample and three individual taxon samples. Lipid content will be determined on the same samples used for PCB congener analysis. All benthic invertebrate samples subject to PCB congener analysis will also be analyzed for lipid content to determine if there is a correlation between the two variables.

3.2.1.5 Water Quality Parameter Analysis

Measurements of water quality parameters (temperature, pH, conductivity and dissolved oxygen) will be made in the field as standard indicators of water quality conditions. Dissolved oxygen values will be converted to percent saturation of dissolved oxygen in order to account for differences in temperature and conductivity. Water quality parameters and other independent variables (e.g., grain-size distribution, total organic carbon, total carbon/total nitrogen, total inorganic carbon, metals) will be used in conjunction with the various dependent variables (e.g., species diversity and abundance) to derive and interpret multiple correlation coefficients. In

addition, physical characteristics, such as depth, approximate flow rate and river width will be recorded in the field.

3.2.1.6 Quantifying Sediment Properties

Sediment sampling for PCB congeners will be conducted in conjunction with the benthic invertebrate sampling. In this regard, benthic invertebrate exposure can be quantified relative to levels of PCBs in the sediment, and will yield data that can be used in a variety of either parametric or non-parametric statistical correlation procedures. Both benthic invertebrates and sediment samples will be taken from a single stratigraphic layer of material, therefore, providing increased confidence in the representativeness of the PCB congener concentrations. All Thompson Island Pool sediment samples will also be analyzed for metals, total organic carbon, total carbon/total nitrogen, total inorganic carbon, and grain-size distribution. The information these parameters will provide, except for metals, are discussed further in the following section, in conjunction within the Upper and Lower Hudson River Sediment and Benthic Invertebrate Study. Only the Thompson Island Pool sediment samples will be analyzed for metals, to determine whether differences in metals concentrations between sampling locations may be affecting the composition of benthic invertebrate communities. Standard USEPA Contract Laboratory Program (CLP) methods will be used.

3.2.2 Upper and Lower Hudson River Sediment and Benthic Invertebrate Sampling Study

The Upper and Lower Hudson River Sediment and Benthic Invertebrate Sampling Study is intended to examine the PCB congener concentrations in sediments along the Hudson River, in ecologically significant areas (many of the sampling stations are designated as significant coastal fish and wildlife habitats by NYSDEC), to estimate potential adverse ecological effects. This study will provide an overview of the PCB contamination potential for bioaccumulation (i.e., a correlation of PCB contamination in sediment with PCB contamination in benthic invertebrates). These data will be used to provide an estimate of PCB contamination in sediments at various locations along the Hudson River (see Figures 3-1 and 3-2 for locations); provide an estimate of PCB exposure to benthic invertebrates in sediments by sampling benthic invertebrates at selected sampling stations; and apply a fish bioaccumulation model (see Final Phase 2 Work Plan, Section 5.2) to estimate PCB concentrations in selected fish species at each sampling station. The model may be verified by comparison to

existing fish data or data collected by the National Oceanic and Atmospheric Administration (NOAA) and NYSDEC for this reassessment.

The Upper and Lower Hudson River Sediment Sampling Study is not intended to provide a definitive picture of PCB congener contamination along the Hudson River. It will, however, examine a number of ecologically significant areas as determined by USEPA, NYSDEC, NOAA and others to evaluate the potential for adverse effects on the biological community. The final sediment sampling locations will be selected based on the criteria outlined in Section 6.

The Upper and Lower Hudson River Study has three quantitative components, in addition to the quantitative field evaluation. These are: 1) quantifying sediment properties at each station, including PCB congener analysis; 2) benthic invertebrate analyses at selected stations; and 3) quantifying water quality parameters at each station. These three components are described below.

3.2.2.1 Quantifying Sediment Properties

Sediment samples will be analyzed for PCB congeners, total organic carbon, total carbon/total nitrogen (TC/TN, 20% of samples [1 sample from each location]), total inorganic carbon (TN/TC, 20% of samples [1 sample from each location]), and grain-size distribution.

Congener-Specific PCB Analysis of Sediments

Congener-specific PCB analysis of sediments is necessary to: 1) relate the sampling results to other aspects of the reassessment including potential PCB source(s), benthic invertebrate analyses congener-specific water column analyses and high resolution sediment coring PCB analyses; and 2) determine the total sediment PCB burden.

Total Organic Carbon (TOC), Total Carbon/Total Nitrogen (TC/TN), and Total Inorganic Carbon (TIC)

Levels of total organic carbon (TOC) in sediment can influence the adsorption of PCBs to sediment particles. The higher the TOC level, the greater the tendency of the PCBs to bind to the sediment, which conse-

quently lowers bioavailability potential. Sources of high TOC levels in the sediment may include wood detritus, which has been shown to contain high PCB levels. Therefore, TOC levels in sediments may have important implications for the aquatic food chain. TOC will be analyzed by the USEPA Region II (L. Kahn) Method to provide a standard measure of the sediment organic carbon content for the purposes of the ecological investigation.

The total carbon/total nitrogen (TC/TN) analysis determines the total concentration of both carbon and nitrogen in the sample, including both organic and inorganic forms. The method utilizes very small (<0.1 gm) samples. The analysis will also provide a measure of the sediment carbon-to-nitrogen ratio. When total inorganic carbon (TIC) levels in sediment are low, the total carbon level will reflect the organic carbon content and provide a measure for either potential PCB contamination or for potential adsorption of PCBs from other media. To obtain TOC levels from TC/TN measurements, TIC will be measured and subtracted from the total carbon level.

Approximately 20% of the Upper and Lower Hudson River Study sediment samples will be analyzed for total carbon/total nitrogen and total inorganic carbon (i.e., one sample from each area of study). The subset of samples analyzed for both TOC and total carbon/total nitrogen plus total inorganic carbon will provide a basis for comparison between the two analyses. Assuming comparability of results are established, the extensive data set including TC/TN and TIC results collected in Phase 2A may also be used to calculate TOC. These Phase 2A TOC data could then be used as needed to supplement the TOC data set collected explicitly for the ecological investigation.

Data from the total carbon/total nitrogen and total inorganic carbon analyses (from both the Thompson Island Pool sediment samples and the Upper and Lower Hudson sediment samples) will also be used to supplement the sediment data collected as part of the confirmatory sampling, high resolution sediment coring and the upcoming low resolution sediment coring programs. An extensive sediment data set is needed in order to provide representative sediment data to be used to characterize the relationship between the carbon:nitrogen ratio and the sediment PCB burden. The carbon:nitrogen (C/N) ratio can be used to indicate the presence of woody material in the organic matter found in the sediments since the C/N ratio in wood (100:1) is substantially larger than that for typical soil or aquatic organic material (20:1). The presence of a high C/N ratio in sediments in the Hudson River below Ft. Edward would suggest that the sediments were associated with the large sediment

transport event which took place in the mid 1970's following the removal of the dam at Ft. Edward. The sediments transported during this period contained large amounts of woody material which were previously trapped behind the dam as a result of the releases from wood processing facilities which historically operated upstream of the dam. Wood cellulose has been historically associated with high levels of PCB contamination in the Upper Hudson and thus an indication of its presence can provide a relative measure of potential PCB contamination in sediments. Using these data in conjunction with the results of the geophysical investigation, confirmatory sampling and low resolution coring, it should be possible to characterize large portions of the river sediments in terms of the organic carbon content and the C/N ratio with the potential for PCB contamination.

Grain-Size Distribution

Sediment samples will be analyzed for grain-size distribution by laser particle analysis. Grain-size distribution data will be used for several purposes. Initially, grain-size from benthic invertebrate stations will be used to determine textural similarity. Second, grain-size distribution is a significant factor affecting the establishment of benthic invertebrate communities. Third, grain-size distribution can affect the propensity of PCBs to bind to the substrata. In general, PCBs are associated with fine-grained particulates.

3.2.2.2 Analysis of Benthic Invertebrates

Benthic invertebrates will be analyzed for congener-specific PCB concentrations, lipid content and biomass at all four of the federally designated Hudson River Estuarine Sanctuaries (Stockport Creek and Flats [RM 123]; Tivoli Bays [RM 100]; Iona Island [RM 40]; and Piermont Marsh [RM 24]). To provide an intermediate station between Tivoli Bays and Iona Island, benthic invertebrates will also be analyzed at the Esopus Meadows Sampling Station (RM 88).

Benthic invertebrates will be quickly sorted to identify the dominant members of the community and then the total sample will be analyzed for PCBs at the congener level. Procedures for congener-specific PCB and lipid analyses of benthic invertebrate are described in Section 3.2.1.3 and 3.2.1.4, respectively.

3.2.2.3 Water Quality Parameter Analysis

Temperature, pH, conductivity, and dissolved oxygen will be measured in the field as standard indicators of water quality conditions. Salinity will also be measured at some of the Lower Hudson stations (below RM 70), where measurable salinity may be present. Physical characteristics, such as depth, will also be recorded.

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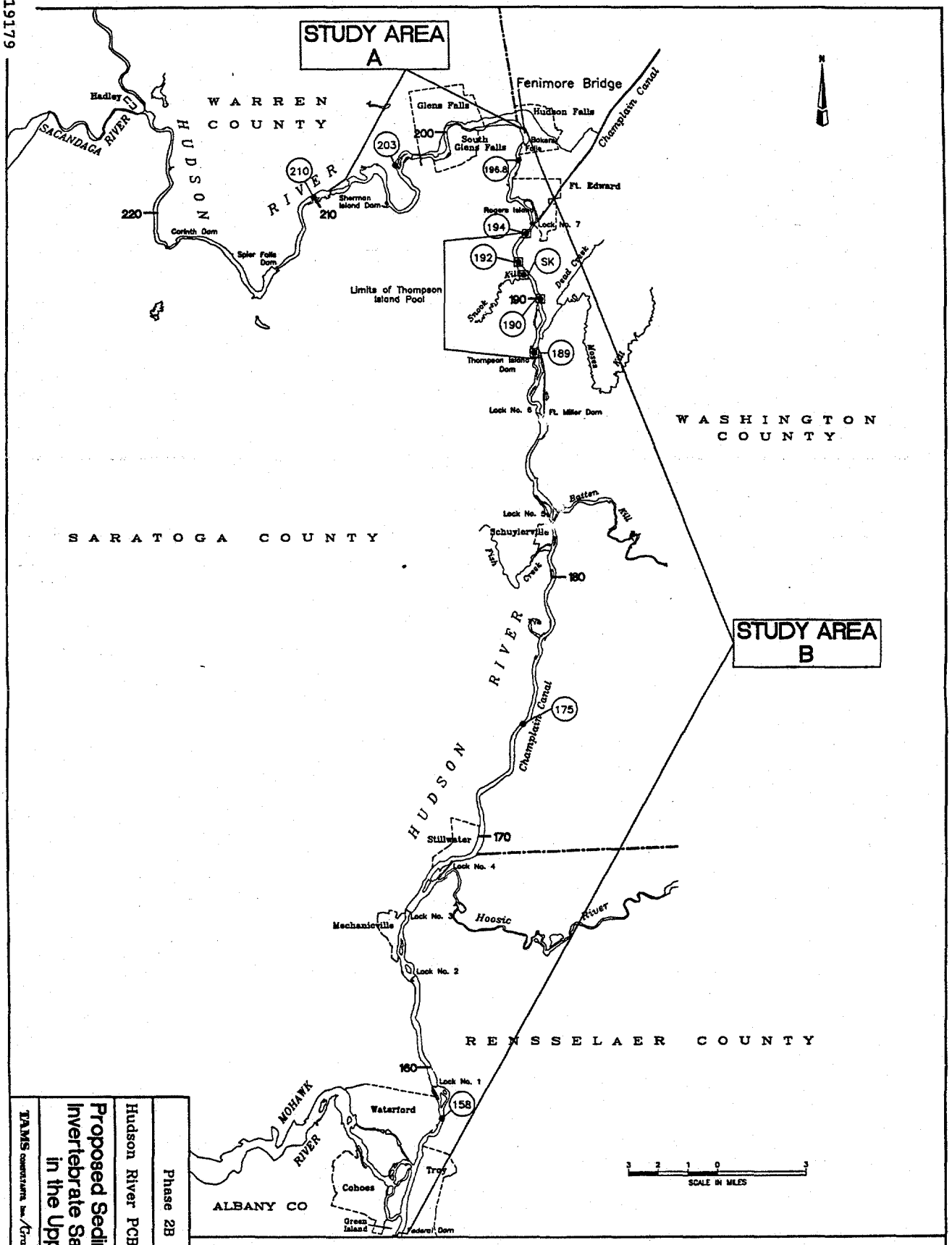

Legend

- 189 — Location of Proposed Sediment Sampling Station
- 188 — Location of Proposed Combined Sediment and Benthic Invertebrate Sampling Station (for Thompson Island Pool Study)
- 180 — River Mile

Note:

1. Study Area A: Sherman Island Dam to Fenimore Bridge
2. Study Area B: Fenimore Bridge to Federal Dam
3. Actual demarcation between Study Areas A and B is just north of Fenimore Bridge so that Study Area B includes the old Hudson Falls Treatment Plant outfall.

Phase 2B Sampling Plan

Hudson River PCB Reassessment RI/FS

Proposed Sediment and Benthic Invertebrate Sampling Locations in the Upper Hudson

TAMS consultants, Inc./Gradient corporation

Figure 3-1

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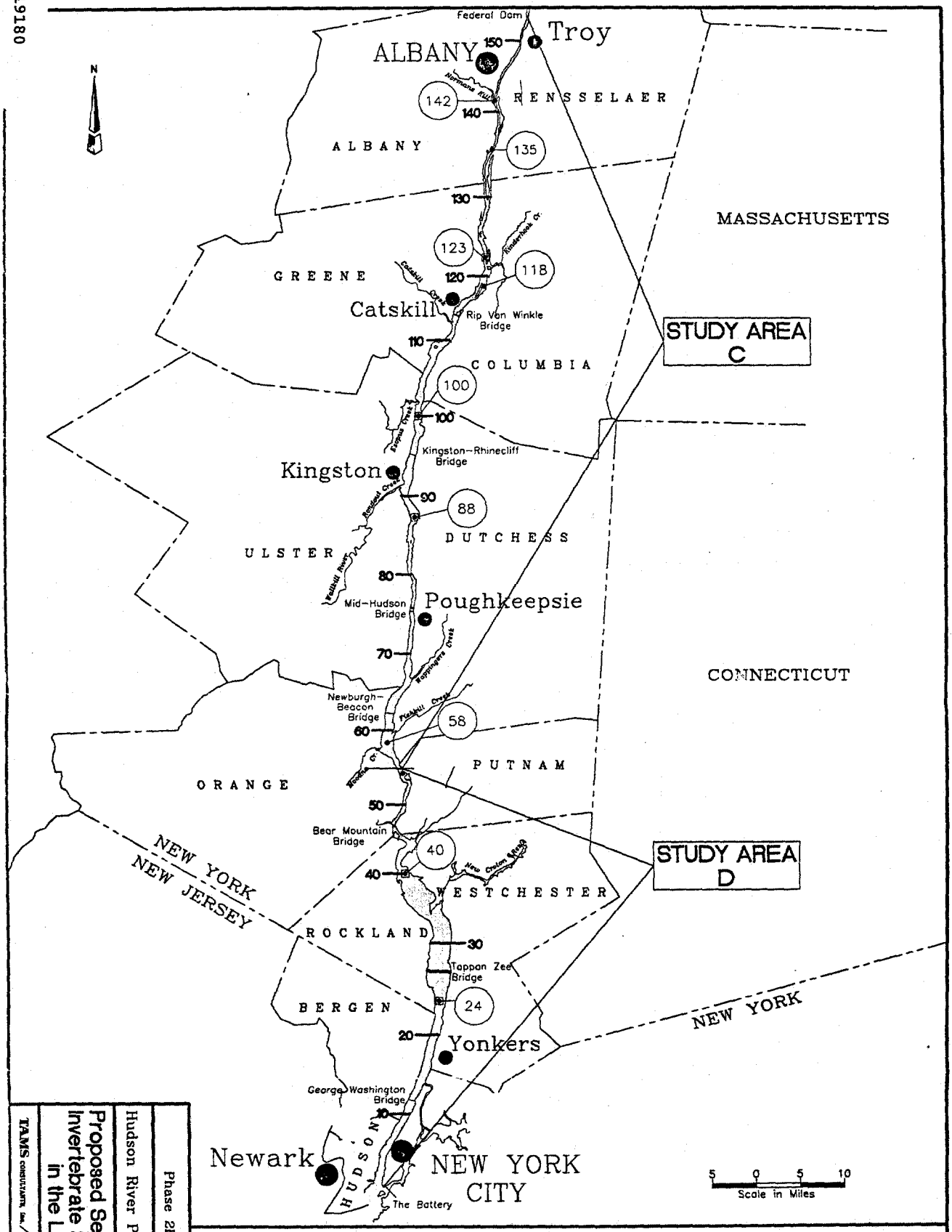


Legend

- 88 — Location of Proposed Sediment Sampling Station
- 88 — Location of Proposed Sediment and Benthic Invertebrate Sampling Station
- 100 — River Mile

Note:

1. Study Area C: Federal Dam to River Mile 55
2. Study Area D: River Mile 55 to The Battery

Phase 2B Sampling Plan

Hudson River PCB Reassessment RI/FS

Proposed Sediment and Benthic Invertebrate Sampling Locations in the Lower Hudson

Figure 3-2

TAMS CONSULTANTS, INC. / Gradient CORPORATION

4 Project Organization

The project team required to perform this remedial investigation will consist of representatives from USEPA Region II, TAMS Consultants, Inc. and Gradient Corporation, technical consultants, subcontractors, and analytical laboratories. A diagram of the Phase 2B Benthic Invertebrate and Sediment Sampling Project Organization is shown in Figure 4-1.

The TAMS Project Manager, Albert DiBernardo, reports directly to Douglas Tomchuk, USEPA's Remedial Project Manager (RPM). TAMS will provide overall project management services for the Phase 2B ecological sampling activities and conduct the field sampling. Gradient Corporation, subcontractors to TAMS, will provide technical consulting services for chemistry, quality assurance oversight, and laboratory activities.

4.1 Operations Responsibility

The TAMS Project Manager (PM), Al DiBernardo, will be responsible for overseeing the activities of the field team, headed by the Field Operations Leader (FOL), Helen Chernoff, who is responsible for proper completion of the tasks included in the Phase 2B SAP/QAPjP. Chris Purkiss will serve as the Field Sampling Coordinator for the benthic invertebrate and sediment sampling efforts. The FOL is responsible for making field decisions regarding field activities and together with the Field Sampling Coordinator, is responsible for the field team maintaining proper sampling, decontamination, and chain-of-custody procedures in collecting benthic invertebrate and sediment samples. Once samples have been collected, the FOL will verify that samples are properly packaged and shipped to the analytical laboratories.

4.2 Laboratory Responsibilities

Laboratories will be contracted by either of two pathways: via a contract with TAMS directly; or contracted through EPA's Sample Management Office (SMO). Laboratories which will be contracted through SMO will be obtained through standard procedures for acquiring laboratories for routine analytical services and special analytical services.

4.2.1 TAMS-Contracted Laboratories

TAMS will contract an analytical laboratory for the PCB congener and lipid analyses. The TAMS/Gradient Quality Assurance Officer, Dr. Dallas Wait, will monitor the activities the TAMS-contracted laboratories. He will be responsible for overseeing the implementation of technical and recording requirements of sample analyses in accordance with this SAP/QAPjP.

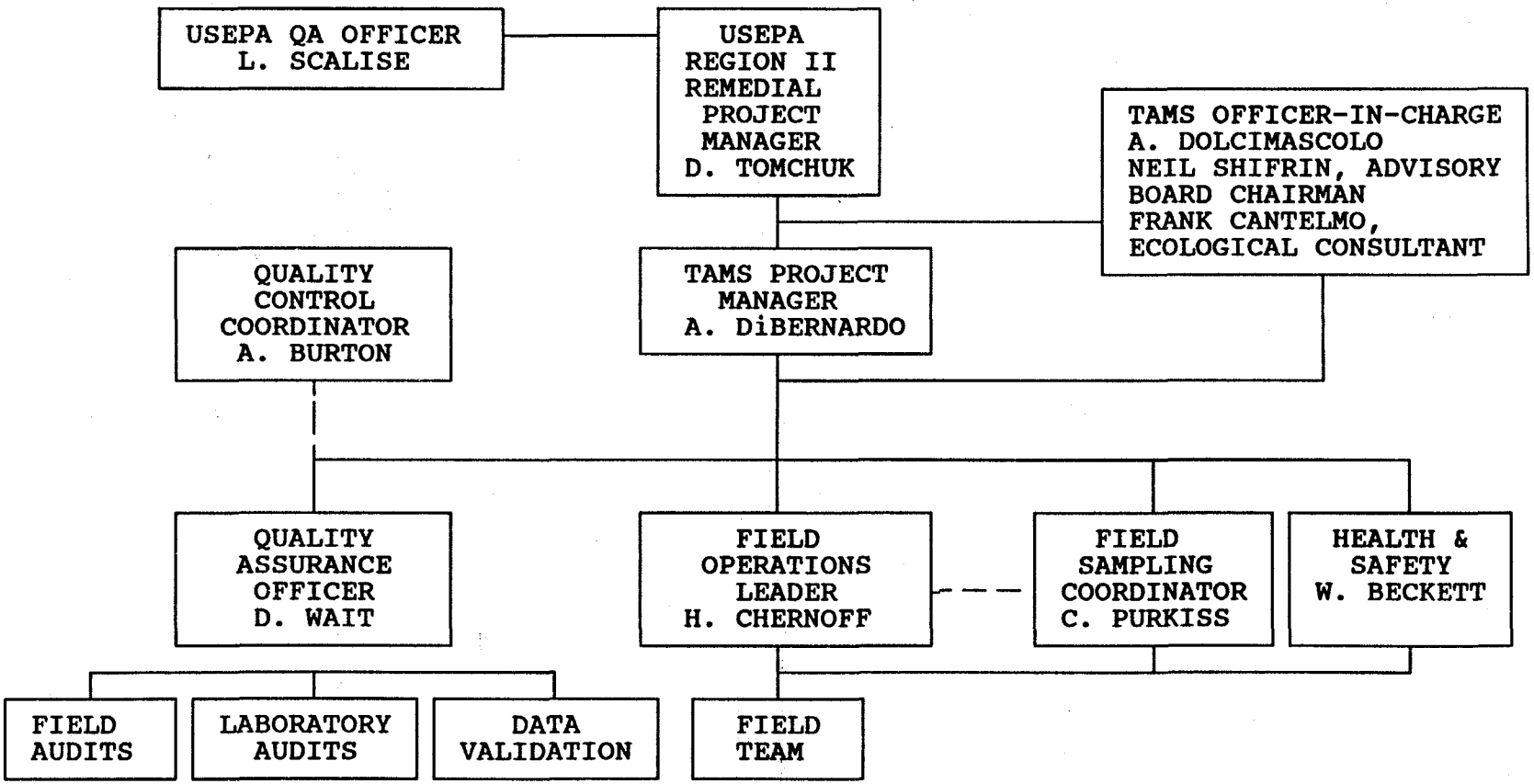
4.2.2 EPA/SMO-Contracted Laboratories

For routine analytical services (e.g., TAL metals) as well as the remaining special analytical services (e.g., total organic carbon) TAMS will obtain a laboratory through the standard Region II procedures. TAMS' responsibility for EPA/SMO-contracted laboratories will consist solely of preparation of the special analytical services (SAS) requests which detail the technical scope of analytical work, and validation of the data generated by these laboratories.

4.3 Quality Assurance Responsibilities

The Field Operations Leader and Field Sampling Coordinator are responsible for maintaining chain-of-custody on all samples collected, as well as verification with sampling team personnel that sampling techniques and quality control procedures are in order and consistent with those detailed in this SAP/QAPjP before initiation of site activities. They are responsible for prompt review and corrective action of any quality control deviations at the site. The project's Quality Assurance Officer will oversee quality control/quality assurance issues for the field operation and the TAMS-contracted laboratories. In addition, each laboratory chosen to perform the analysis will have its own QA Director to monitor internal quality control. EPA's Region II Quality Assurance Officer, Laura Scalise, will be involved with the approval of this SAP/QAPjP, and then monitor the implementation of the plan.

FIGURE 4-1
HUDSON RIVER REASSESSMENT RI/FS
PHASE 2B BENTHIC INVERTEBRATE AND SEDIMENT SAMPLING PROJECT ORGANIZATION



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5 Quality Assurance Objectives for Measurement of Data

As was the case in Phase 2A, the primary objective of the Quality Assurance (QA) program is to provide data of sufficient quality and quantity to achieve the objectives as stated in Section 3. Data quality and quantity are measured through comparison of resulting data with established acceptable limits for data precision, accuracy, representativeness, comparability, and completeness (PARCC) as described in "Data Quality Objectives for Remedial Response Activities" USEPA/540/G-87-003. Analytical sensitivity, evidenced by the method detection limit, is also an important consideration for this project, especially for congener-specific PCB analysis. Data that have certain aspects that may be outside PARCC QA objectives will be evaluated to determine what, if any, aspects of the data can be defensibly used to meet the RI/FS objectives. Objectives for the PARCC and sensitivity parameters for this RI/FS are described in this section.

5.1 PARCC Objectives

PARCC parameter and sensitivity objectives have been developed for sediments and biota based on sample objectives, analytical methods, historical data (examined in a qualitative sense) and published guidelines for EPA's Contract Laboratory Program (CLP), as listed in Section 17 (References).

Tables 5-1 and 5-2 contain PARCC and sensitivity objectives for the laboratory and field analyses respectively. PARCC parameter and sensitivity objectives should be achieved through the use of standardized sample collection and analysis procedures.

5.1.1 Precision

Precision measures the reproducibility of data or measurements under specific conditions. Precision is a quantitative measure of the variability of a group of data compared to their average value. Precision is usually stated in terms of relative percent difference or relative standard deviation. Measurement of precision is dependent upon sampling technique and analytical method. Both sampling and analysis will be as consistent as possible. For the laser grain size analysis, precision will be stated in terms of percent similarity. Percent similarity is the sum of the lower percents of each (diameter) band-size in a sample pair. For further discussion on percent similarity see Section 14.1.

Quality control (QC) samples, including field and laboratory duplicate samples, and matrix spike and matrix spike duplicate samples will be analyzed and used to measure precision. An additional measure of precision for PCB congener analyses is the comparison of surrogate recoveries between the unspiked, matrix spike, and matrix spike duplicate sample aliquots. A one-in-twenty frequency per matrix will receive a laboratory duplicate analysis (inorganics) and matrix spike/matrix spike duplicate (organics analyses). In general, field blanks will be collected at a frequency of one per decontamination event for each type of sampling equipment. The maximum frequency of field blanks will be one per matrix per day during a continuous sampling event in which the same equipment is used and decontaminated repeatedly. The minimum frequency of field blanks will be one per matrix per week.

Field duplicates/replicates will be collected once for every 20 samples per matrix. Field duplicate/replicate results will be evaluated during data validation. It should be noted that the precision objectives shown on Table 5-1 are guidelines. In accordance with Region II data validation protocols, data may be fully usable even if these objectives are not met.

5.1.2 Accuracy

Accuracy is a measure of the bias in a measurement system which may result from sampling or analytical error. Sources of error that may contribute to poor accuracy include laboratory error, sampling inconsistency, field contamination, laboratory contamination, handling, matrix interference, and preservation. Field blanks, surrogate spikes, performance evaluation (PE) samples, laboratory control samples (inorganics) as well as matrix spike QC samples, will be used to measure accuracy for project samples.

5.1.3 Representativeness

Representativeness expresses the degree to which sample data represent the characteristics of the media or matrix from which it is collected. Samples that are considered representative are ones that are properly collected to accurately characterize the nature and extent of contamination at a given location. Representativeness will be measured by using the methods (e.g. sampling, handling, and preserving) specified in this SAP/QAPjP (see Section 6). Comparison of the analytical results from field replicates will provide a

direct measure of individual sample representativeness. Field replicates will be collected once for every 20 samples for the benthic invertebrate and sediment matrices.

5.1.4 Comparability

Comparability is a qualitative parameter expressing the confidence with which data sets can be compared. Comparability requires similarity of sampling, analytical methods and matrix, as well as precision and accuracy to be within appropriate QC limits before the data can be used for unqualified comparison of data sets. This will be accomplished through the consistent use of the analytical and sampling methods described in Section 6. Specifically, quantitative and qualitative information on comparability will be obtained for the GC/ECD PCB congener analyses in 10% of the sediments using GC/ITD confirmation (Appendix A-5). Additionally, quantitative information on comparability will be obtained for TOC - L. Kahn method and TOC calculated from TC/TN and TIC results.

5.1.5 Completeness

Completeness is defined as the percentage of data that is judged to be valid to achieve the objectives of the investigation compared to the total amount of data collected. Deficiencies in the data may be due to sampling techniques, poor accuracy or precision, or matrix effects, laboratory error. While these deficiencies may affect certain aspects of the data, usable data may still be extracted from applicable samples.

5.1.6 Sensitivity

Quantitation limits for analyses scheduled for the Phase 2B effort are specified in Section 9.0 of this SAP/QAPjP. Quantitation limits may be affected by matrix interferences, such as those caused by highly contaminated samples. In a case in which method specified detection limits are not achieved for PCB congener analyses, sample/extract cleanups will be performed. If the quantitation limits are still not achievable, the usability of the data, with respect to meeting the Phase 2B objectives, will be evaluated.

5.2 Procedures for Monitoring PARCC Parameters

PARCC parameters will be monitored through the use of procedures which have been referred to in Section 5.1. These procedures will include the use of field blanks, laboratory method blanks, field and laboratory duplicates or replicates, matrix spikes, duplicate matrix spikes, surrogate spikes, performance evaluations, laboratory control samples, and a careful examination of all calibration and check standards. Laboratory Control Samples (LCSs) and PE samples are samples containing a known or true value which the laboratory prepares and analyzes concurrently with project samples. LCSs and PE samples are useful in judging analytical accuracy.

5.3 Field Measurements

Measurement data will be generated in many field activities that are incidental to collecting samples for off-site analytical testing or in activities unrelated to sampling. These activities include, but are not limited to, the following:

- Documenting time and weather conditions;
- Locating and determining the depth of sampling stations;
- Determining pH, dissolved oxygen, specific conductance, and temperature (and salinity in the Lower Hudson only) of sampling locations; and
- Screening of PCB levels in sediments by immunoassay.

The general QA objective for field measurement data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the intended use of the data through the documented use of standardized procedures. The procedures for performing these activities and the standardized formats for documenting them are presented in Section 6 and Appendices C-1 through C-5 of this SAP/QAPjP.

Table 5-1

Accuracy and Precision Objectives for Laboratory Analyses

Parameter	Matrix	Field Replicate (Duplicate) Precision (% RPD)	Sample/MD or MS/MSD[1,2] Precision (% RPD)	LCS[3] Accuracy (% Recovery)	MS/MSD[2] Accuracy (% Recovery)	Surrogate[4] Accuracy (% Recovery)
PCB Congeners	Tissue	50	40	60-150	60-150	60-150
	Sediment	50	40	60-150	60-150	60-150
TAL Metals	Sediment	100 or Diff <2xCRDL	50 or Diff <2xCRDL	within specified control limits[5]	75-125	NA
Total Organic Carbon	Sediment	100 or Diff <2xRL	≤25[6]	80-120	NA	NA
Total Carbon/Total Nitrogen	Sediment	100 or Diff <2xRL[7]	50	80-120	NA	NA
Total Inorganic Carbon	Sediment	100 or Diff <2xRL	50	80-120	NA	NA
Grain-Size (laser)	Sediment	80[8]	NA	NA	NA	NA
Lipid Content	Tissue	50	50	NA	NA	NA

[1]PCB congener analyses will have 10% sediments confirmed by GC/ITD, Appendix A-5, with criteria of <75% RPD between methods.
[2]MS/MSD required for PCB congeners only. TAL metals and other parameters require a matrix duplicate (MD).
[3]LCS (Laboratory Control Sample) is equivalent to the ICV (Instrument Calibration Verification) for conventional parameters
[4]Surrogates are tetrachloro-meta-xylene (TCMX) and octachloronaphthalene.
[5]Analyte-specific LSC recoveries are specified in the CLP statement of work for Inorganics Analysis.
[6]Precision for quadruplicates is ±3SD, or ±25%, whichever is lower.
[7]Carbon/Nitrogen ratio must not vary by more than 10%.
[8]Grain-size precision criterion expressed as percent similarity, which is the sum of the lower percents of each diameter band-size in a sample pair.

Notes:
- RPD = Relative Percent Difference
- CRDL = Contract Required Detection Limit
- NA = Not Applicable
- RL = Analyte - specific Reporting Limit
- MD = Matrix Duplicate Sample
- MSD = Matrix Spike Duplicate Sample
- MS = Matrix Spike Sample
- SD = Standard Deviation

Table 5-2

Accuracy and Precision Objectives for Field Analyses

Measurement	Instrument	Precision	Accuracy
pH	Corning Model 103	±0.1 pH units	0.1 pH units
	Hanna HI 9025	±0.1 pH units	0.1 pH units
Conductivity	YSI Model 33	±10/25/250 umho/cm[1]	±5/25/250 umho/cm[1]
Temperature	YSI Model 33	±0.1°C	±0.1°C or 1% (whichever is greater)
Salinity	YSI Model 33	±0.2 ppt	±6.5% of reading
Dissolved Oxygen	YSI Model 51B/57[2]	0.1 mg/l	±0.1 mg/l at full scale
PCB Immunoassay	EnSys PCB RISc	Soil Test System	> 80%[3]

[1] Depends on scale being used.

[2] Operation and specifications of the YSI Model 51B and YSI Model 57 dissolved oxygen meters, either of which may be used for this project, are essentially identical.

[3] Field Immunoassay compared to laboratory GC PCB data studies indicated accuracy (i.e., absence of false positives/false negatives) at pre-set screening level to range from 82% to 99%.

6 Sampling and Design of Benthic Invertebrate and Sediment Studies

6.1 Design of Benthic Invertebrate and Sediment Studies

The Phase 2B ecological sampling program is divided into two separate sampling events: the comprehensive Thompson Island Pool Benthic Invertebrate and Sediment Study; and a more general Upper and Lower Hudson River Sediment and Benthic Invertebrate Study at selected stations in ecological significant areas along the Hudson River.

6.1.1 Thompson Island Pool Benthic Invertebrate and Sediment Sampling Study

The Thompson Island Benthic Invertebrate and Sediment Sampling Study is designed to investigate the macroinvertebrate community at four selected stations within the Thompson Island Pool and at an additional control area. Data generated will be used to determine statistically significant relationships, if any, between sediment PCB congener concentrations and community structure and bioaccumulation. Additional parameters, such as grain-size distribution and TOC, will also be examined to determine their relationship to PCB concentrations and community structure. The sampling design consists of taking five replicate samples within an approximate 10 meter by 10 meter grid at each station. Field screening for PCBs will be performed prior to collecting samples for laboratory analyses as an aid in identifying sampling locations with a wide range of PCB concentrations. Table 6-1 lists the approximate number and type of samples to be collected during Phase 2B activities.

Sampling stations will be selected based on the following criteria:

- Sampling stations will be located in shallow zones no greater than 3 meters total depth;
- Stations will be located in comparable areas, as determined by a station's physical and other characteristics and the professional judgement of an experienced staff biologist(s) (see Figures 6-1 and 6-2);

- Stations will be located in areas containing fine-grained sediments high in organic matter. The results of the geophysical investigation and the confirmatory sampling program (Phase 2A) will be used to guide the station selection process. In this manner, stations will be limited to areas of similar textural qualities;

- To the extent possible, stations will be located in areas of elevated PCB levels, based on the 1984 NYSDEC sediment surveys (NYSDEC, 1988) of the Thompson Island Pool;

- Approximate concentrations of PCBs levels in the sediment will be confirmed by field analysis prior to sampling for laboratory analysis is conducted; and

- In addition, two of the Thompson Island Pool Sampling stations will be located in areas where NYSDEC/NOAA fish sampling may occur[1].

The proposed Thompson Island Pool sampling stations are located at RM 194, 192, 190, 189, and the control area at the mouth of Snook Kill (approximately RM 191.5).

6.1.2 Upper and Lower Hudson River Sediment and Benthic Invertebrate Sampling

The Upper and Lower Hudson River Sediment Study is designed to examine PCB congener concentrations in ecologically significant areas along the Upper and Lower Hudson River. Data collected in this study will allow an evaluation of the potential effects of PCBs on the biological community in various areas of the Hudson River. Table 6-2 lists the approximate number and type of samples to be collected during Phase 2B activities. The sampling design consists of taking replicate samples within a 10 meter by 10 meter grid at each of the 14 locations. In addition, benthic invertebrates will be analyzed for PCB congeners at the four federally designated Hudson River Estuarine Sanctuaries and one additional station. Data from these samples will be

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[1] NYSDEC/NOAA has proposed the following 16 locations for their fish sampling program: RM 210, RM 203, RM 196.8, RM 194, RM 189, RM 175, RM 158, RM 142, RM 135, RM 123, RM 115-118, RM 99-103, RM 88, RM 58, RM 40 and RM 24. Efforts will be made to coordinate TAMS' sediment, benthic invertebrate and fish sampling to include the NYSDEC/NOAA sampling stations. Sediment and benthic samples will be analyzed even if NYSDEC/NOAA do not collect the fish samples.

evaluated in conjunction with the NYSDEC/NOAA fish sampling effort to assess the potential effects of PCBs in ecologically important or sensitive habitats.

Sampling stations will be selected on the following criteria:

- Sampling stations will be located in shallow zones, no greater than 3 meters total depth;
- Only stations with fine-grained sediments and organic material will be selected, thereby limiting stations to areas sharing similar textural qualities;
- Sampling stations will be located in areas where NYSDEC or NOAA fish sampling may occur[2];
- Only stations reflecting mainstream conditions, rather than those at the mouths of tributary streams, will be selected;
- Field screening of PCBs in the sediment may be performed prior to selecting the location of some sampling station. Locations with high levels of PCBs will receive preference as sampling areas; and
- Sampling areas in the Lower Hudson were selected according to NYSDEC designation as significant coastal fish and wildlife habitats. Therefore, sampling stations will be located in ecologically significant locations.

The proposed Upper and Lower Hudson River sampling stations are located at RM 210, 203, 196.8, 175, 158, 142, 135, 123, 118, 100, 88, 58, 40 and 24.

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[2] See Footnote 1 on previous page

6.1.3 Data Interpretation and Statistical Analyses

Initial statistical methods employed may include various non-parametric (e.g., Kruskal-Wallis test, Friedman's method for randomized blocks) and parametric (e.g., single classification, two-way ANOVA) procedures. Statistical analyses will be used to determine if there are significant differences between the various invertebrate stations with respect to species diversity, biomass, pH, temperature, conductivity, dissolved oxygen, grain-size distribution, total organic carbon, metals, PCB congener levels in benthic invertebrates and PCB congener levels in sediments.

Variables found to be significantly different will be retained and analyzed by various multivariate techniques including factor analysis.

The goal of the multivariate approach will be to determine the minimum number of independent variables needed to account for most of the variance in the original set of retained variables. Multivariate techniques are used extensively in order to identify and isolate a number of causal factors that may be responsible for observed differences in biological communities. For example, factor analysis produces a correlation matrix and a factor pattern in which shifts in either benthic community structure or bioaccumulation may be related to and explained by differences in PCB congener levels.

Faunal affinity between sites will be determined by the Bray-Curtis similarity measure. Species diversity will be assessed by the Shannon-Wiener diversity index (H'). In addition, an equitability index (H'/H max) will be used in order to relate maximum theoretical diversity to actual diversity.

6.2 Field Sampling and Measurement

Field measurements (Section 6.2.1) for this program include field screening of sediments for PCBs, and collection of water samples for water quality parameter measurements. Sediment and benthic invertebrate samples will also be collected for various chemical, geotechnical, and biological parameters (Section 6.2.2).

6.2.1 Field Measurements

6.2.1.1 Field PCB Screening

To select appropriate areas for sampling, field screening for PCBs will be performed at all the benthic invertebrate sampling stations, and at least 50% of the sediment sampling stations. The PCB RISC® Soil Test is a semi-quantitative test that gives an absence/presence indication around one or two detection levels. For example, sediments can be tested to determine if concentrations are above 1 ppm; if the test is positive they can then be tested at a higher detection limit, for example, 10 ppm. The testing device exhibits recognition of major commercial Aroclors (as PCBs) and conforms to EPA SW-846 Draft Method 4020 for screening for PCBs using immunoassay detection. The estimated number of samples to be screened in the field is 10 per station. It is anticipated that the PCB field screening procedure in the Thompson Island Pool sampling effort will reject approximately two of the initial five stations. Therefore, two additional stations will be sampled yielding a total of seven stations, requiring 70 PCB screening samples (10 samples x 7 stations). For the Upper and Lower Hudson River Sediment Study, PCB field screening will be performed at approximately half of the stations (10 samples x 6 stations) yielding an estimated total of 60 screening samples. Since the total PCB concentrations expected in the Lower Hudson (results obtained from the high resolution coring program, 1.0 to 1.5 ppm) are close to the detection limits of the PCB field screening test, the test will only be conducted at some of the stations. The screening test has different detection limits for specific Aroclors (0.4 to 4.0 ppm), some of which are above expected PCB concentrations in the Lower Hudson. If after several attempts with the screening test PCBs are not detected, the sampling locations will be selected based on the other criteria described above (Section 6.1). Additional detail on the performance of the PCB field screening is provided in Appendix C-5.

6.2.1.2 Water Quality Parameter Measurements

Field measurements of water quality parameter (temperature, pH, conductivity, and dissolved oxygen) will be made of all sampling locationss in the Thompson Island Pool and in this Upper and Lower Hudson River Measurements of these parameters will be taken by lowering the instrument probe through the water column to approximately one meter above the top of the sediment. The instruments (see Table 5-2) will be equipped with extended cables (10' or longer) so the measurement can be taken in situ.

6.2.2 Sampling Procedures

Once a sampling location has been selected, three separate grabs are required to obtain adequate quantities for each sample in the Thompson Island Pool Study, and two separate grabs are required for the Upper and Lower Hudson River Sediment study. The grab samples will be subdivided for the specified analyses as described below.

1. One grab will be initially sub-sampled for PCB congener sediment analysis and then sieved. The benthic invertebrates collected will be analyzed for PCB congeners, biomass and lipid content.

2. One grab will be sub-sampled for TOC, TAL metals, grain-size, and TC/TN and TIC, if designated.

3. One grab will provide benthic macroinvertebrates for the abundance and diversity analysis. This benthic macroinvertebrate grab sample (abundance and diversity) will be collected for the Thompson Island Pool study only.

If an inadequate amount of sample is obtained in any of the grabs, an additional grab(s) will be taken, as needed. In addition, one sample of epibenthic organisms will be collected at each station. Epibenthic organisms will be analyzed for PCB congeners, lipid content and biomass. Epibenthic organisms will be collected from an area adjacent to the grab samples, after grab sampling has been completed. This procedure allows both benthic and epibenthic samples to be collected from undisturbed areas.

An Ekman grab sampler (15 cm x 15 cm x 15 cm) will be used to collect all samples, except epibenthic organisms. Ekman grabs are lightweight and useful for sampling soft, finely divided substrates from sand to silt/clay. The Ekman grab encloses a square equal in area from surface to maximum depth of penetration before closure. In soft substrates the penetration is quite deep and the angular closure of the spring loaded jaws has little impact on the volume of sample collected. For example, if the depth of penetration is 5 cm, the organisms lying at that depth have the same opportunity to be sampled as those above. In order to collect only one depositional layer, the Ekman grab will be examined upon retrieval and only those samples that are 2/3 full and

in which the stratigraphy of the sediment is maintained will be used. Samples will be taken one to five meters apart, depending on field conditions. Epibenthic organisms will be collected using a fine mesh dip net attached to a pole.

The following procedures will be used to collect material for benthic invertebrate and sediment samples at each sampling station for the two studies.

1. Select a sampling location. Approximate sampling grids will be 10 meters by 10 meters in area. Drive a pole to mark each corner and string a line between the poles for boat orientation. Record the location as precisely as possible in log book, using shoreline markers and detailed project maps that contain east and north coordinates.

2. Position the boat and stabilize it over the sampling location.

3. Attach a clean decontaminated Ekman grab sampler to extension poles, so that the river bottom can easily be reached.

4. Set the trip mechanism and lower the Ekman grab sampler to the river bottom. Push the grab no more than 15 centimeters into the sediments. Trip the grab sampler.

5. Pull the Ekman grab sampler back up to the boat and drain all water.

6. Gently open the top of the Ekman grab sampler so as to minimize disturbance of the sediments obtained.

7. Visually examine the sample to determine if an adequate sample was obtained and that sediment stratigraphy was not badly disturbed. If so, proceed to step 8, if not, rinse the apparatus with river water and return to step 3 if the area has not been excessively disturbed. If the area was extremely disturbed, return to step 1.

8. Insert a pre-cleaned glass coring syringe into the upper 5 cm of sediment and remove a sediment sub-sample for PCB congener analysis. Repeat four times for a total of five samples, using the same syringe and use the composite sub-sample for PCB sediment congener analysis. The sample should be thoroughly composited in the laboratory prior to extraction and analysis. Rinse the glass syringe with river water and set aside for use in step 11.

9. If a benthic invertebrate sample for PCB congener analysis is required, insert plastic "mini-cores" (diameter 4.7 cm) to a depth of 5 cm and extrude into a modified bucket with a U.S. Standard No. 30 sieve fitted to the bottom. Repeat four times for a total of five mini-cores. Slowly add analyte-free water to rinse the sediment off the benthos until sample is completely clean (i.e., no visible sediment particles remain in the benthic invertebrate sample). Waste water will be collected in a large plastic temporary holding bucket, to minimize impact on subsequent samples. Place sample into pre-cleaned, labelled jar. If an insufficient number of benthic invertebrates is collected (e.g., <1 gram), increase the number of "mini-cores" or return to step 3. As an alternative, if the biologist present deems it appropriate, epibenthic invertebrates may be collected using a dip net and substituted for the benthic invertebrate sample. Factors such as species abundance and total biomass will determine whether epibenthic samples will be used to supplement benthic sampling. If no benthic sample is required, skip to step 11.

10. Place excess sediment in temporary holding bucket (to avoid sediment being redeposited on subsequent samples) and then rinse Ekman grab with river water until visibly clean and rinse once with potable or deionized water. If necessary, move the boat to the next sample collection point within the sampling-station grid. Perform steps 4 through 7 and proceed to step 11.

11. Insert the glass coring syringe into the upper 5 cm of sediment and remove a sediment sample for TOC analysis and for TAL metals TC/TN and TIC analyses, if required. Remove five or more full syringes of material and place directly into appropriate sample jars. If adequate material remains for grain-size analyses, collect material using the glass syringe. If an insufficient amount of material remains, repeat steps 3 through 7, and then proceed to collect material for grain-size distribution analysis.

12. If a benthic invertebrate sample for identification and biomass is required, repeat steps 3-7. If the previous sampling efforts have disturbed the river bottom, it will be necessary to reposition the boat slightly. Insert plastic "mini-cores" (diameter 4.7 cm) to a depth of 5 cm and extrude into a modified bucket with a U.S. Standard No. 30 sieve fitted to the bottom. Repeat four times. Slowly add water until sample is completely clean (i.e., no visible sediment particles). Waste water will be collected in a large plastic bucket, to minimize impact on subsequent samples. Place rinsed sample into a clear, labeled sample container for macroinvertebrate identification and biomass. Preserve sample by adding a solution of 95% ethyl alcohol containing 125 mg/l rose bengal stain. Sample sorting and identification procedures will follow those described in Appendix B-8 (which are consistent with those described by NYSDEC, 1991). If no benthic invertebrate sample is required then skip to step 13.

13. Move boat if no undisturbed sampling area is accessible. Collect one sample of epibenthic organisms by gently moving a dip net above the river bottom. Place the sample into a labeled glass jar. Repeat until adequate sample (at least 1 gram) is obtained.

14. After completing the five sets of replicate samples at each station, return excess sediments and wastewater to the river and rinse holding buckets and Ekman grab sample in river water until visibly clean.

15. Field Duplicates - Field duplicates for all parameters will be collected at a minimum frequency of 5%. Field duplicates for the various parameters will be collected by filling two sets of sample containers alternately as described in steps 8 through 12, above. For organisms, double weight (i.e., 2 grams) will be collected and then split.

6.2.3 Field Personnel

Thompson Island Pool Field sampling teams will consist of, at a minimum, a biologist and a geologist, with additional staff as needed. The Upper and Lower Hudson River Sediment and Benthic Invertebrate Study field sampling teams will consist of at least a biologist and a geologist, with additional staff as needed.

6.3 Sample Containers, Preservation, and Holding Times

The specific containers, preservatives and holding times to be used are presented in Table 6-3.

6.4 Preparation of Sampling Equipment and Containers

6.4.1 Decontamination of Sampling Equipment

Decontamination and subsequent use of decontaminated equipment will be documented in a field notebook. If visual signs such as discolorations indicate that the decontamination process was insufficient, the equipment will be decontaminated again. If the situation persists, the equipment will be replaced.

Field decontamination of syringes and other glass and stainless steel materials used for sample collection will consist of rinsing with potable or deionized water, followed by an acetone rinse and distilled deionized analyte free water rinse. After decontamination, stainless steel and glass materials will be dried and wrapped in aluminum foil.

Decontamination of the plastic mini-cores used for subsample benthic organisms will consist of verifying that the mini-core is visibly clean, followed by a final rinse with potable or deionized water.

Decontamination of the Ekman grab sampler will consist of verifying that the instrument is visibly clean, followed by a final rinse with potable or deionized water.

6.4.2 Preparation of Sample Containers

Glass and plastic sample containers will be purchased precleaned and used with no further clean-up. Sample containers will be precleared in accordance with USEPA protocols and documentation appropriate to container use (e.g., Eagle-Picher Level 1).

6.5 Sample Handling and Shipment

All benthic invertebrate and sediment samples collected in the field, with the exception of grain-size distribution samples, will be shipped by on ice an overnight carrier (or delivered directly by TAMS personnel) to the appropriate laboratory within one day of sample collection. Only two shipments of grain-size distribution samples will be sent to a laboratory, as there is no holding time for this analysis. Samples for grain-size analysis will not be preserved or chilled. TAMS will supply the shipping coolers.

All sample containers will be properly labelled prior to shipment. At a minimum the sample label will contain:

- The Investigation Name (Hudson River Phase 2B)
- Field Sample Number
- Sample Tag number
- Date and Time Collected
- Matrix
- Sampler's Name
- Preservatives Added (if applicable)
- Analysis Parameters
- Remarks

Chain-of-custody procedures are detailed in Section 7. Protocols for shipping samples are found in Appendix C-1.

Table 6-1

Approximate Number of Samples to be Collected for Thompson Island Pool Benthic Invertebrate and Sediment Sampling Study During Phase 2B

Analytical Procedure	Benthic Sampling (5 Stations, 5 repl. each; plus 1 epibenthic grab per station)	Sediment Sampling (5 stations, 5 repl. each)
PCB Congeners	30-105[a]	25
TAL Metals	--	25
Total Organic Carbon	--	25
Total Carbon/Total Nitrogen	--	25
Total Inorganic Carbon	--	25
Grain-Size (Laser Particle)	--	25
Lipid Content	30-105[a]	--
Diversity and Abundance	25	--
Biomass	30-105[a]	--

Note: Sample estimates do not include QA/QC samples (e.g., field duplicates, blanks, etc.).

[a]Number of samples to be analyzed is dependent upon number of taxa collected in adequate numbers for individual analyses.

Table 6-2

Approximate Number of Samples to be Collected for the Upper and Lower Hudson River Sediment Sampling and Benthic Invertebrate Study During Phase 2B

Analytical Procedure	Benthic Sampling (5 Stations, 5 repl. each; plus 1 epibenthic grab per station)	Sediment Sampling (14 stations, 5 repl. each)
PCB Congeners	30	70
Total Organic Carbon (TOC)	--	70
Total Carbon/Total Nitrogen (TC/TN)	--	14[a]
Total Inorganic Carbon (TIC)	--	14[a]
Grain-Size (Laser Particle)	--	70
Lipid Content	30	--
Biomass (benthic invertebrates)	30	--

[a]One sample for TC/TN and TIC analysis will be collected at each of the 14 stations

Note: Sample estimates do not include QA/QC samples

Table 6-3
Sample Containers, Preservation and Holding Times

Parameter	Matrix	Holding Time*	Container	Preservative	Sample Size
PCB Congeners	Sediment	7/40 days**	45 ml glass jar, teflon lined cap	maintain at 4°C	5-10 grams
	Benthic and Epibenthic Invertebrates	7/40 days**	45 ml glass jar, teflon lined cap	maintain at 4°C	1 gram
	Aqueous (Field Blanks Only)	7/40 days**	1 liter glass jar, teflon lined cap	maintain at 4°C	1 liter
Grain-Size	Sediment	none	500 ml glass jar	None	500 grams
TAL Metals	Sediment	28 days Mercury; 180 days all others	500 ml glass jar, teflon-lined cap	maintain at 4°C	250 grams
	Aqueous (Field Blanks Only)	28 days Mercury, 180 days all others	1 liter glass jar, teflon lined cap	HNO_3 to pH $\leq$2, maintain at 4°C	1 liter
Total Organic Carbon	Sediment	14 days	500 ml glass jar	maintain at 4°C	100 grams
	Aqueous (Field Blanks Only)	28 days	250 or 500 ml glass jar, teflon lined cap	H_2SO_4 to pH $\leq$2, maintain at 4°C	25 ml
Total Carbon/Total Nitrogen	Sediment	none	45 ml glass jar	maintain at 4°C	5-10 mg
Total Inorganic Nitrogen	Sediment	none	45 ml glass jar	maintain at 4°C	5-10 mg
Species Diversity and Abundance	Benthic Invertebrates	none	500 ml jar	95% ethanol and rose bengal stain	1-10 grams
Biomass	Benthic Invertebrates	none	500 ml jar	95% ethanol and rose bengal stain	Variable
Lipid Content	Benthic and Epibenthic Invertebrate Extract***	none***	N/A***	N/A***	5 ml***

* Holding time calculated from time of sample collection.
** First number is time until extraction; second number is time after extraction until analysis.
*** Lipid content determination is performed on an aliquot of the hexane extract for congener-specific PCB analysis of benthic invertebrates.

FIGURE 6-1
PHYSICAL CHARACTERISTICS/WATER QUALITY FIELD DATA SHEETS*
(Page 1 of 2)

Site Location/RM Number:

Landmarks:

WEATHER CONDITIONS:

PHOTOGRAPH NUMBERS:

OBSERVATIONS AND/OR SKETCH:

RIPARIAN ZONE/ INSTREAM FEATURES

Predominant Surrounding Land Use (forest, field/pasture, residential, commercial, industrial, etc.):

Local Watershed Erosion: ____ None ___ Moderate ____ Heavy

Local Watershed NPS Pollution: ____ No Evidence ____ Some Potential Source ____ Obvious Source

Estimated River Width: _____ m Estimated River Depth: ____ m

High Water Mark: ____ m Estimated Velocity: ____

Dam Present: ____ Yes ____ No Channelized: ____ Yes ____ No

SEDIMENT/SUBSTRATE

Sediment Odors (e.g., normal, sewage, petroleum, chemical, anaerobic, none, other):

Sediment Oils: ____ Absent ____ Slight ____ Moderate ____ Profuse

PCB Field Screening Results (if performed):_____

Sediment Deposits (e.g., sludge, sawdust, paper fiber, sand, relict shells, other):

Are the undersides of stones which are not deeply embedded black? ____ Yes ____ No

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* Adapted from USEPA, 1989. Rapid Bioassessment Protocols for Use in Streams and Rivers, Benthic Macroinvertebrates and Fish. EPA/440/4-89/001, Office of Water (WH-553).

FIGURE 6-1 (pg 2 of 2)

SEDIMENT/SUBSTRATE (Continued)

Inorganic Substrate Components

Substrate Type	Diameter	% Composition in Sampling Area
Bedrock		
Boulder	>256 mm	
Cobble	64-256 mm	
Gravel	02-64 mm	
Sand	0.06-2.00 mm	
Silt	0.004-0.06 mm	
Clay	<0.004 mm	

Organic Substrate Components

Substrate Type	Characteristic	% Composition in Sampling Area
Detritus	Sticks, Wood, Coarse Plant Materials (CPOM)	
Muck-Mud	Black, Very Fine Organic Materials (VFOM)	
Marl	Grey, Shell Fragments	

WATER QUALITY

Temperature ____° Dissolved Oxygen ____ pH ____

Conductivity _____ Other: _____

Instruments Used:_____

Water Odors (e.g., normal, sewage, petroleum, chemical, none, other): _____
Water surface Oils (e.g., slick, sheen, globs, flecks, none):

Turbidity: ____ Clear ____ Slightly Turbid ____ Opaque

Water Color:_____

FIGURE 6-2
BIOSURVEY FIELD DATA SHEET
RAPID BIOASSESSMENT PROTOCOL

Relative Abundance of Aquatic Biota

Periphtyon	0	1	2	3	4
Filamentous Algae	0	1	2	3	4
Macrophytes	0	1	2	3	4
Slimes	0	1	2	3	4
Macroinvertebrates	0	1	2	3	4
Fish	0	1	2	3	4

0 = Absent/Not Observed 1 = Rare 2 = Common 3 = Abundant 4 = Dominant

MACROBENTHOS QUALITATIVE SAMPLE LIST

Group	Relative Abundance	Comments/ Observations
Coleoptera		
Crustacea		
Diptera: Chiron.		
Diptera: Misc.		
Ephemeroptera		
Megaloptera		
Mollusca		
Odonata		
Oligocheata		
Plecoptera		
Tricoptera		
Other		

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7 Chain-of-Custody Procedures

An essential part of any sampling/analytical program is the ability to document the history of samples. This is begun as soon as the samples are in custody. A sample is in custody when it meets any one of the following requirements:

- It is in your actual possession, or
- It is in your view after being in your physical possession, or
- It was in your possession, and then you locked or sealed it to prevent tampering, or
- It is in a secure area.

Chain-of-custody establishes the documentation and control necessary to identify and trace a sample from collection to final analysis. Such documentation includes labeling to prevent mix-up, container seals to prevent unauthorized tampering with contents, secure custody, and the necessary records to support potential litigation. These precautions are crucial for a valid chain-of-custody. It is policy to follow the USEPA sample custody or chain-of-custody protocol as described in "NEIC Policies and Procedures," EPA-330/9-78-001-R, revised May 1986. This custody is in three parts: field sample collection and custody; laboratory custody; and final evidence files. Final evidence files, including all originals of laboratory reports, are maintained under document control in a secure area. The original laboratory reports will be placed in the final evidence files after completion of the final report.

7.1 Sample Identification

In order to properly track all samples collected for the ecological investigation, a 10 character alphanumeric identification system will be used. This system is based on earlier sampling efforts (e.g., high resolution coring and water column sampling). The sample numbering system will provide a quick source of information on sample type and is being followed for all sample collection.

The sample numbering format is defined as follows:

AA-A00-0000A

where "A" represents a letter and "0" represents a number.

The first two characters represent the sampling effort. For this sampling effort, all samples will be labelled EC (ecological). The next group of alphanumeric characters consists of a single letter which represents the matrix (S for sediment; B for benthic invertebrate; E for epibenthic invertebrate; and A for aqueous) and a two digit station location number. Stations will be numbered from 01 to 19, beginning at RM 210 and ending at RM 24 (see Table 7-1).

The last four digits will be used to differentiate between samples at each sampling station. For example, the first replicate will be 0001, the second replicate will be 0002, and so on. The last alphanumeric character is used to designate field duplicates (D), matrix spike samples (M) (this designation also applies to samples designated for matrix duplicate and matrix spike duplicate analysis), or field blanks (B).

For example, sample number EC-S02-0003 would be the third replicate sediment sample taken at RM 203 (second northernmost station) for the ecological sampling program. Samples collected in separate containers for individual analyses (e.g., PCB congener, TOC, etc.) will be recorded in the field log book and marked on the chain-of-custody forms.

7.2 Field Specific Custody Procedures

Sampling team personnel will perform the sampling and will retain custody until shipment to the laboratory. One chain-of-custody form will be used for each sample shuttle (cooler) shipped to the laboratory. Figure 7-1 provides a sample of a chain-of-custody form.

The field activities will be recorded daily in a serialized field logbook. The following information will be recorded in the logbook used at this site:

- Specific sample location.
- Sampling personnel.
- Date and time of sample collection.
- Sample number, airbill number, seal number.

- Sampling conditions, i.e., sample matrix, weather on-site, type of sampling container and preparation, description of sampling procedure, preservation, and shipping.

The sample packaging and shipment procedures, detailed in Appendix C-1 and summarized below, will be performed so that the samples will arrive at the laboratory with the chain-of-custody intact.

Field custody procedures will be as follows:

- The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples.

- All bottles will be labelled and tagged with sample numbers and locations.

- Sample tags will be completed for each sample using waterproof ink.

- The Field Operations Leader must review field activities to determine whether proper custody procedures were followed during the field work.

Transfer of custody and shipment procedures will be as follows:

- Samples will be accompanied by a properly completed chain-of-custody form. The sample numbers and locations will be listed on the chain-of-custody form. When transferring the possession of samples, the individuals relinquishing and receiving should sign, date, and note the time on the record. This record documents transfer of custody of samples from sampler to another person, to a mobile laboratory, to the permanent laboratory, or to/from a secure storage area.

- Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with the completed, signed chain-of-custody form enclosed in each sample box or cooler. Shipping containers will be secured with strapping tape or duct tape and custody seals for shipment to the laboratory. The preferred procedure includes use of a custody seal attached

to the front right and front left of the cooler. The custody seals will be covered with clear plastic tape. The cooler will be strapped shut with strapping or duct tape in at least two locations.

- All shipments will be accompanied by the chain-of-custody record identifying the contents. The original record will accompany the shipment, and a copy will be retained by the Field Operations Leader.

- If the samples are sent by common carrier, an airbill or bill of lading will be used. Receipts of airbills will be retained as part of the permanent documentation. Commercial carriers are not required to sign off on the custody form, as long as the custody forms are sealed inside the sample cooler, and the custody seals remain intact.

7.3 Laboratory Custody Procedures

Samples will be received by the laboratory sample custodian. Samples will be unpacked and inspected for the following:

- Broken or leaking bottles
- Presence of all samples listed on field chain-of-custody
- Bottle labels match field chain-of-custody
- Presence of ice and temperature of cooler
- Number of coolers received matches number shown on airbill

The sample custodian of TAMS-contracted laboratories is required to fill out a Sample Receiving Checklist Form (Figure 7-2) or equivalent. If problems or discrepancies are noted, they will be documented on this form. Discrepancies in the number of samples received or sample bottle labels will also be documented on the field chain-of-custody form. The sample custodian will then sign and date the field chain-of-custody form.

After accepting custody of the samples, the sample custodian will log in the samples. Each sample will be assigned a unique sequential laboratory number which will be used for tracking the sample through the

laboratory. The field chain-of-custody, inspection report, and airbill will then be forwarded to the laboratory project manager.

The laboratory project manager or designee will inspect the paperwork. If problems are noted, the laboratory project manager will resolve them with the TAMS QC coordinator, Mr. Allen Burton.

After log-in, samples will be placed in refrigerated storage pending analysis. Sample chain-of-custody is maintained throughout the laboratory by a system of door locks. Access will require use of a key issued to company employees. Thus, in order to gain access to the samples, one must either be an employee or be escorted by an employee.

7.4 Final Evidence File

The final evidence file for the project will consist of: laboratory data packages (summary and raw data from the analysis of QC samples and investigative samples, chromatograms, mass spectra, calibration data, worksheet, sample preparation, chain-of-custody record); logs; field logbooks; photographs; and subcontractor reports. All reports will be retained by EPA Region II.

FIGURE 7-1
CHAIN-OF-CUSTODY RECORD

EPA — United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Special Analytical Service
Packing List/Chain of Custody

SAS No.

1. Project Code / Account Code	2. Region No. / Sampling Co.	4. Date Shipped / Carrier	6. Sample Description (Enter In Column A) 1. Surface Water 2. Ground Water 3. Leachate 4. Rinsate 5. Soil/Sediment 6. Oil 7. Waste 8. Other (Specify)	7. Preservative (Enter in Column C) 1. HCl 2. HNO_3 3. $NaHSO_4$ 4. H_2SO_4 5. NaOH 6. Other (SAS) (Specify) 7. Ice only N. Not preserved
Regional Information	Sampler (Name)	Airbill Number		
Non-Superfund Program	Sampler Signature	5. Ship To		
Site Name	3. Type of Activity: Lead / Pre-Remedial / Remedial / Removal SF / PRP / ST / FED — PA / SSI / LSI — RIFS / RD / RA / O&M / NPLD — CLEM / REMA / REM / OIL / UST			
City, State / Site Spill ID				

Sample Numbers	A Matrix Enter from Box 6	B Conc Low Med High	C Preservative Used from Box 7	D Analysis	E Sample used for spike and/or duplicate	F Regional Specific Tracking Number or Tag Number	G Station Location Identifier	H Mo/Day/Year/Time Sample Collection	I Sampler Initials	J Designated Field QC
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
Shipment for SAS complete? (Y/N)										

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks Is custody seal intact? Y/N/none	

Split Samples ☐ Accepted (Signature)
☐ Declined

EPA Form

DISTRIBUTION:
White - Region Copy Yellow - SMO Copy Pink - Lab Copy for Return to SMO Gold - Lab Copy

S 004856

Note: This form is used for Special Analytical Services (SAS) laboratories procured through the USEPA Sample Management Office (SMO) Forms used for Routine Analytical Services laboratories procured through USEPA-SMO, and for laboratories contracted directly by TAMS, may vary.

FIGURE 7-2
SAMPLE RECEIVING CHECKLIST

Control #: _____ Date Received: _____
Job Code: _____ Date Inspected: _____
Inspected by: _____ Time Inspected: _____
(print name)

Paperwork	Yes	No	Intact	**Broken**
Airbill	_____	_____		
Cooler Custody Seals:	_____	_____	_____	_____
Bottle Custody Seals:	_____	_____	_____	_____
Chain-of-Custody:	_____	_____		
Traffic Reports:	_____	_____		
Sample Tags:	_____	_____		
Tags Listed on COC:	_____	_____		

Sample Condition	Cool	Warm	Hot	Degrees C
Cooler Temperature:	_____	_____	_____	_____

	Yes	No	
Ice:	_____	_____	Melted
Bottles Broken:	_____	_____	
Bottles Leaking:	_____	_____	

Preservation pH: (record measured pH)	_____ OK	_____ Not OK	_____ Not Checked
Other _____:	_____	_____	

Shipment Condition:	_____ OK	_____ Not OK	_____ Major	_____ Minor

Problems and Comments

_____

_____

_____

_____

_____ _____
Signature Date

TAMS/*Gradient*

Table 7-1

Ecological Sample Location Designations

Station Location	Numerical Designation
RM210	01
RM203	02
RM196.8	03
RM194	04
RM192	05
RM191.5 (Snook Kill)	06
RM190	07
RM189	08
RM175	09
RM158	10
RM142	11
RM135	12
RM123	13
RM118	14
RM100	15
RM88	16
RM58	17
RM40	18
RM24	19

8 Calibration Procedures and Frequency

8.1 Field Instruments

Field personnel will follow the procedures described in the instrument manufacturer's instructions and the SOPs in Appendices C-2 through C-6 so that measurements during the investigation have been collected with properly calibrated instruments. Field equipment will be calibrated at the frequency shown on Table 8-1, and maintained and repaired in accordance with manufacturer's specifications. In addition, prior to use, each major piece of equipment will be cleaned, decontaminated, checked for damage, and repaired as needed. These activities will be noted in the field log notebook.

Despite even the most rigorous maintenance program, equipment failures do occur. When equipment cannot be repaired in the field, it will be replaced as quickly as possible.

Quality control efforts, accuracy and precision objectives for field measurement equipment are summarized in Section 11. Calibration procedures and frequency for field instruments are summarized in Table 8-1. Specific detailed methods of calibration for the following instruments are presented in the appendices as follows:

Instrument	Appendix
pH Meter	C-2
Dissolved Oxygen Meter	C-3
Salinity/Conductivity/Temperature Meter	C-4
Colorimeter (PCB Immunoassay)	C-5

8.2 Laboratory Calibration

The analytical methods selected for use in this investigation specify the types and frequency of calibrations. The specific calibration requirements are delineated within the methods provided in the following references:

Parameter	Reference/Appendix
PCB Congeners (GC/ECD)	A-4
PCB Congeners (GC/ITD Confirmation)	A-5
Total Carbon/Total Nitrogen	B-3
Total Inorganic Carbon	B-4
Extraction and Cleanup of Waters (PCB congeners - field blanks)	A-1
Extraction and Cleanup of Sediments (PCB congeners)	A-3
Extraction and Cleanup of Benthic Invertebrates (PCB congeners)	A-8
Lipid Content	A-8
Grain-Size Distribution (laser method)	B-5
Total Organic Carbon in Sediment (TOC)	B-7
TOC - Water (field blanks)	USEPA MCAWW 415.1
TAL Metals (sediment and field blanks)	CLP ILMO2.1

MCAWW: Methods for Chemical Analysis of Water and Wastes, EPA/600-4-020, Revised 1983.

Table 8-1

Field Equipment Maintenance and Calibration Protocols

Equipment	Maintenance/Calibration	Frequency
pH meters (Corning 103 or Hanna HI 9025)	Calibrate with two pH buffer solutions (pH 7.0 and 10.0)	Daily before use. Check at pH 7.0 every 4 hours
Temperature	As per manufacturer's instructions	Once per day before use
Specific conductance (YSI-SCT 33)	Calibration verified as per manufacturer's instructions. Recalibration, if necessary, will be performed by manufacturer	Once per day before use
Salinity (YSI-SCT 33)	Calibration verified as per manufacturer's instructions. Recalibration, if necessary, will be performed by manufacturer	Once per day before use
Dissolved oxygen meter (YSI 51B or YSI 57)	Calibration according to manufacturer's recommendations with ambient air	Once per day before use
Rechargeable equipment batteries	Charge.	After use as required
Sampling accessories	Periodic maintenance performed and recorded in equipment maintenance log	As required
PCB Immunoassay (Colorimeter)	As per manufacturer's instruction	Once per sample analysis group

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9 Analytical Procedures

To accomplish the objectives of the RI/FS, laboratory analyses will be performed for PCB congeners, TAL metals, total organic carbon, total carbon/total nitrogen, total inorganic carbon, grain-size distribution (laser method), lipid content of biomass, biomass and species diversity and abundance. In addition, a field screening analysis for PCBs in sediments by immunoassay will be performed. A summary of the methodologies to be employed is included in Table 9-1. Table 9-2 provides a listing of the PCB congeners to be analyzed for in Phase 2B and Table 9-3 defines the detection limit goals for the PCB congeners and the other conventional parameters which will meet the data quality objectives of the program.

Table 9-1

Analytical Procedures

Parameter	Method	Appendix
PCB Congeners	GC/ECD	A-4
PCB Congeners Confirmation	GC/ITD	A-5
Total Organic Carbon - Sediment	USEPA Region II (L. Kahn)[1]	B-7
Total Organic Carbon - Aqueous[2]	USEPA MCAWW 415.1[3]	--
Total Carbon/Total Nitrogen	Verardo, 1990	B-3
Total Inorganic Carbon	[Project - Specific]	B-4
Grain-Size Distribution	Laser Particle	B-5
Biomass, Species Diversity and Abundance	NYSDEC[4]	B-8
PCB Level in Sediments (Immunoassay)	USEPA Draft Method 4020[5]	C-5
TAL Metals	CLP ILM02.1[6]	--
Lipid Content	[Project-Specific]	A-8

[1] Determination of Organic Carbon in Sediment, Lloyd Kahn, USEPA Region II, July 1988.
[2] The only aqueous samples to be analyzed are field blanks associated with sediment samples.
[3] Methods for the Chemical Analysis of Water and Wastewater, USEPA-600/4-79-020, Revised 1983.
[4] NYSDEC. 1991. Quality Assurance Plan for Biological Stream Monitoring in New York State.
[5] Ensys PCB Concentration Determination by Immunoassay, SW-846 Draft Method 4020.
[6] USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis, Document Number ILMO2.1, September 1991.

Table 9-2

PCB Congeners

BZ#	PCB Congener
1	2-Chlorobiphenyl
2	3-Chlorobiphenyl
3	4-Chlorobiphenyl
4	2,2'-Dichlorobiphenyl
5	2,3-Dichlorobiphenyl
6	2,3'-Dichlorobiphenyl
7	2,4'-Dichlorobiphenyl
8	2,4'-Dichlorobiphenyl
9	2,5-Dichlorobiphenyl
10	2,6-Dichlorobiphenyl
12	3,4-Dichlorobiphenyl
15	4,4'-Dichlorobiphenyl
16	2,2',3-Trichlorobiphenyl
18	2,2',5-Trichlorobiphenyl
19	2,2',6-Trichlorobiphenyl
22	2,3,4'-Trichlorobiphenyl
25	2,3',4-Trichlorobiphenyl
26	2,3',5-Trichlorobiphenyl
27	2,3',6-Trichlorobiphenyl
28	2,4,4'-Trichlorobiphenyl
29	2,4,5-Trichlorobiphenyl
31	2,4',5-Trichlorobiphenyl
37	3,4,4'-Trichlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl
41	2,2',3,4-Tetrachlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
53	2,2',5,6'-Tetrachlorobiphenyl
56	2,3,3',4'-Tetrachlorobiphenyl
66	2,3',4,4'-Tetrachlorobiphenyl
70	2,3',4',5-Tetrachlorobiphenyl
75	2,4,4',6-Tetrachlorobiphenyl
77	3,3',4,4'-Tetrachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl
83	2,2',3,3',5-Pentachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl
85	2,2',3,4,4'-Pentachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl
92	2,2',3,5,5'-Pentachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl
97	2,2',3',4,5-Pentachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl
105	2,3,3',4,4'-Pentachlorobiphenyl
107	2,3,3',4',5-Pentachlorobiphenyl
115	2,3,4,4',6-Pentachlorobiphenyl
118	2,3',4,4',5-Pentachlorobiphenyl
119	2,3',4,4',6-Pentachlorobiphenyl
122	2',3,3',4,5-Pentachlorobiphenyl
123	2',3,4,4',5-Pentachlorobiphenyl
126	3,3',4,4',5-Pentachlorobiphenyl
128	2,2',3,3',4,4'-Hexachlorobiphenyl
129	2,2',3,3',4,5-Hexachlorobiphenyl
136	2,2',3,3',6,6'-Hexachlorobiphenyl
137	2,2',3,4,4',5-Hexachlorobiphenyl
138	2,2',3,4,4',5'-Hexachlorobiphenyl
141	2,2',3,4,5,5'-Hexachlorobiphenyl
149	2,2',3,4',5',6-Hexachlorobiphenyl
151	2,2',3,5,5',6-Hexachlorobiphenyl
153	2,2',4,4',5,5'-Hexachlorobiphenyl
157	2,3,3',4,4',5'-Hexachlorobiphenyl
158	2,3,3',4,4',6-Hexachlorobiphenyl
167	2,3',4,4',5,5'-Hexachlorobiphenyl
170	2,2',3,3',4,4',5-Heptachlorobiphenyl
171	2,2',3,3',4,4',6-Heptachlorobiphenyl
177	2,2',3,3',4',5,6-Heptachlorobiphenyl
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
185	2,2',3,4,5,5',6-Heptachlorobiphenyl
187	2,2',3,4',5,5',6-Heptachlorobiphenyl
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
190	2,3,3',4,4',5,6-Heptachlorobiphenyl
191	2,3,3',4,4',5',6-Heptachlorobiphenyl
193	2,3,3',4',5,5',6-Heptachlorobiphenyl
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
196	2,2',3,3',4,4',5',6-Octachlorobiphenyl
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
199	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
201	2,2',3,3',4',5,5',6-Octachlorobiphenyl
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
208	2,2',3,3',4,,5,5',6,6'-Nonachlorobiphenyl
209	Decachlorobiphenyl

Note: BZ# = Ballschmitter and Zell System.

Table 9-3

PCB Congeners and Conventional Parameter Detection Limits Goals

PCB Congeners

Matrix	Homolog	Detection Limit
Benthic and Epibenthic Invertebrates (approx. 1 gram)	Monochlorobiphenyl	4-8 µg/kg
	Dichlorobiphenyl through Hexachlorobiphenyl	2-4 µg/kg
	Heptachlorobiphenyl through Decachlorobiphenyl	2-4 µg/kg
Sediment (approx. 2 grams)	Monochlorobiphenyl	1-2 µg/kg
	Dichlorobiphenyl through Hexachlorobiphenyl	0.5-1 µg/kg
	Heptachlorobiphenyl through Decachlorobiphenyl	0.5-1 µg/kg
Water (1-2 field blanks)	Monochlorobiphenyl	1-2 ng/l
	Dichlorobiphenyl through Hexachlorobiphenyl	0.5-1 ng/l
	Heptachlorobiphenyl through Decachlorobiphenyl	0.5-1 ng/l

Conventional Parameters

Parameter	Detection Limit
Total Organic Carbon - Sediment	0.01% weight (100 mg/kg)
Total Organic Carbon - Water (field blanks)	1.0 mg/l
Total Carbon	0.02% weight (200 mg/kg)
Total Inorganic Carbon	0.02% (200 mg/kg)
Total Nitrogen	0.001% weight (10 mg/kg)
Grain-Size - Laser Particle Method	>4 mm to 1 μm distribution
PCB Concentration by Immunoassay	$\geq$0.4 ppm for Aroclors 1254 and 1260; $\geq$1 ppm for Aroclor 1248; $\geq$2 ppm for Aroclor 1242; and $\geq$4 ppm for Aroclors 1232 and 1016
Lipid Content	0.2% Lipids (based on 1 g sample)
Metals	As per CLP SOW ILMO2.1

Notes:

*Dilutions due to high concentration samples or matrix interferences may be necessary. In such cases, reported detection limits will be multiplied by the dilution factor and may exceed limits tabulated.

10 Data Reduction, Validation, and Reporting

Protocols for data reduction and reporting are summarized in Figure 10-1. All field data will be entered into bound serialized notebooks. Originals of field notebooks, chain-of-custody forms, field data sheets, and laboratory reports will be filed and stored. These documents are tracked during a periodic inventory during audits performed under the direction of the TAMS/Gradient Quality Assurance (QA) Officer of the project, Dr. A. Dallas Wait. See Section 18 for definitions of abbreviations employed in the following section.

10.1 Data Reduction

The analyst who generates the analytical data has the prime responsibility for the correctness and completeness of the data. All data will be generated and reduced following protocols specified in the appendices to this SAP/QAPjP or in laboratory SOPs for standard methods. Each analyst will review the quality of his/her work, based on an established set of guidelines. This will constitute the "primary review". The analyst will review the data package to verify that:

- Sample preparation information is correct and complete;
- Analysis information is correct and complete;
- The appropriate SOPs have been followed;
- Analytical results are correct and complete (including calculations);
- QC sample results are within established control limits;
- Blanks are within established control limits;
- Special sample preparation and analytical requirements have been met;
- Documentation is complete (e.g., all anomalies in the preparation and analysis have been documented; holding times are documented, etc.);
- All corrections on raw data and any generated forms are made with a single-line cross-out and initialed and dated by the analyst.

The primary analyst will initial and date all documents generated by him/her. A "secondary review" of the data generated by the primary analyst will be performed. This will entail a spot-check of the above listed items.

Any errors found will trigger a 100% check of all data included in that item. The secondary reviewer will initial and date all reviewed documents.

Data reduction will include provision of periodically updated summary tables containing the following information to the Quality Assurance Officer:

- Collection Date
- Sample Identification Number
- Sample Description
- Sample Location
- Laboratory Number
- Parameter
- Concentration and units
- Analysis Date

Interpretation of raw data and calculation of results are signed and dated by the laboratory scientist performing the data reduction on the data report forms. Another scientist, often the laboratory manager, must verify the results and sign the data before it is released. Additionally, a member of the laboratory QA staff should perform an audit of 5% of the data generated.

10.2 Data Validation

Data validation is the process of reviewing data and accepting, qualifying, or rejecting it on the basis of sound criteria. The data generated during this program must be validated according to established guidelines in this SAP/QAPjP and the USEPA Region II data validation SOPs (USEPA, 1992). Given the non-standard methods contained in this SAP/QAPjP, the data validation approach must consist of a systematic review of the results, associated quality control methods and results, and other supporting data using professional judgment in areas not specifically addressed by EPA guidelines. For the PCB congener analyses, specific data validation SOPs have been developed to address the low level detection limit requirements of GC/ECD (Appendix A-6) and the congener confirmation by GC/ITD. For all other parameters, the data validation will address the following (as appropriate):

- Completeness:

The data package for each Sample Delivery Group (SDG) must include the following items.

1. Traffic Report and Chain-of-Custody (COC) forms.

2. Case narrative listing non-compliance issues.

3. Cover page; tabulated QC results and sample results. At a minimum these will include: tabulated sample concentrations; MS/MSD/MD results with % recoveries and % RPD per analyte; all blanks tabulated (method blanks and laboratory blanks); LCSs with % recoveries; ICVs and CCVs with % recoveries; % solids for sediments; surrogate recoveries; and method detection limits. Additional details are listed in Section 10.3 entitled Data Reporting.

4. Raw data supporting all analyses.

5. Raw data supporting all standardizations, calibrations and QC samples.

6. Preparation or extraction logs for all tests, matrices and samples.

7. % solids determination log (sediments only).

8. Laboratory and field sample IDs are consistent and can be tracked throughout data.

9. Holding times are documented.

- Accuracy

Review of laboratory control samples (LCS) and matrix spike (MS) samples (where applicable) to determine accuracy based on % recovery of a known spiked compound.

$$\%\ recovery = \frac{(spiked\ sample\ value - sample\ value)}{spike\ added} \times 100\%$$

- Precision

Review of laboratory matrix duplicates (MD), matrix spike duplicates (MSD) and field duplicates (FD) where applicable. Based on relative percent difference (RPD) between the duplicate values.

$$RPD = \frac{sample\ value - duplicate\ value}{\left(\frac{sample\ value + duplicate\ value}{2}\right)} \times 100\%$$

For grain-size data (laser method), precision will be evaluated as percent similarity (not RPD), as described in Section 14.1.

- Detection Limits

Review of data reporting limits with SAP/QAPjP specific requirements.

- Blank Contamination

Review of all blanks (field blanks, method/prep blanks, laboratory analytical blanks) to assess validity of the data based on criteria set for blank levels in the SAP/QAPjP.

The data acceptance limits for LCS, MS/MSD, MD, all blanks, ICVs and CCVs are defined within the methods and this SAP/QAPjP.

It is imperative that quantitation limits be kept as low as possible for PCB congener analyses. It is expected that the quantitation limits defined in Section 9 will be met. Precision and accuracy requirements have been defined in Section 5. Guidelines for acceptable surrogate standard recoveries in both biological tissue and sediments, spike recoveries and RPD of duplicates have been defined in this SAP/QAPjP based on EPA Region II and National Functional Guidelines criteria and technical references as listed in Section 17. These guidelines will be used in evaluating data quality.

In addition to the above directives, protocols from the following documents will be used to validate the inorganic and organic data:

1. CLP Organics Data Review and Preliminary Review. January 1992, SOP No. HW-6, Rev. #8. USEPA Region II.

2. Evaluation of Inorganic Data for the Contract Laboratory Program (CLP). January 1992, SOP No. HW-2, Rev. XI, USEPA Region II.

3. Validation SOPs Appendices A-6 and A-7.

4. National Functional Guidelines for Organic Data Review, 1991.

10.3 Data Reporting

For PCB congener data, appropriate CLP forms (modified as necessary) for pesticide/PCB reporting should be used where applicable. The specific deliverables are defined in the applicable SOP or SAS request. Sufficient QC, supporting, and raw data shall be provided so that validation of the data can be performed. In general, data reports for each sample analyzed will include the following information:

- Final analyte concentration.

- Laboratory sample ID#, field sample ID#, location.
- Percent solids (for sediment samples).
- Final volume of extract or prepared sample.
- Preparation or extraction and analysis dates for holding time verification.
- Calibration information, including (where applicable):
  - calibration curve
  - correlation coefficient, and
  - concentration response data of the calibration check standards.
- Results of the second column chromatography check including chromatograms (PCB analysis only).
- Amount of surrogate spiked and percent recovery of each surrogate.
- For matrix spike samples, the amount spiked and % recovery of each compound or analyte spiked.
- For matrix duplicate or spike duplicate samples, % RPD calculated for each compound or analyte.
- For laboratory control samples (or matrix spike blanks), true values and % recovery of each analyte quantitated.
- Blank results for method blanks, field blanks, and laboratory analytical blanks.
- All raw data, preparation and extraction logs must include:
  - analyst initials and date
  - initial and final sample volumes or weights
  - sample description artifacts (e.g. stones, standing water in sediment samples, color)
  - amount and concentration of stock spike solutions added to MS/MSD or LCS samples
  - Vendor or Lot Number identification for all initial and continuing check samples and true value concentrations of these check standards (ICV, CCV, etc.).
- All raw data analysis printouts and logs must include:
  - analyst initials and date
  - Model Number and type of instrument used for analysis
  - conditions of instrument (e.g. wavelength for colormetric analyses, retention times for GC, etc.)
  - time of start of analysis, time for all QC samples, time of end of analysis
  - Method Number or SOP reference
  - dilutions performed and amount of sample analyzed or injected

- calibration standards labeled and time recorded
- QC samples and blanks clearly labeled.

All sediment data will be reported on a dry-weight basis. For sediment data, the % solids of the sample must be reported with the dry-weight sample results.

FIGURE 10-1
PROTOCOLS FOR DATA REDUCTION AND REPORTING:
CONVENTIONAL RAS/SAS LABS

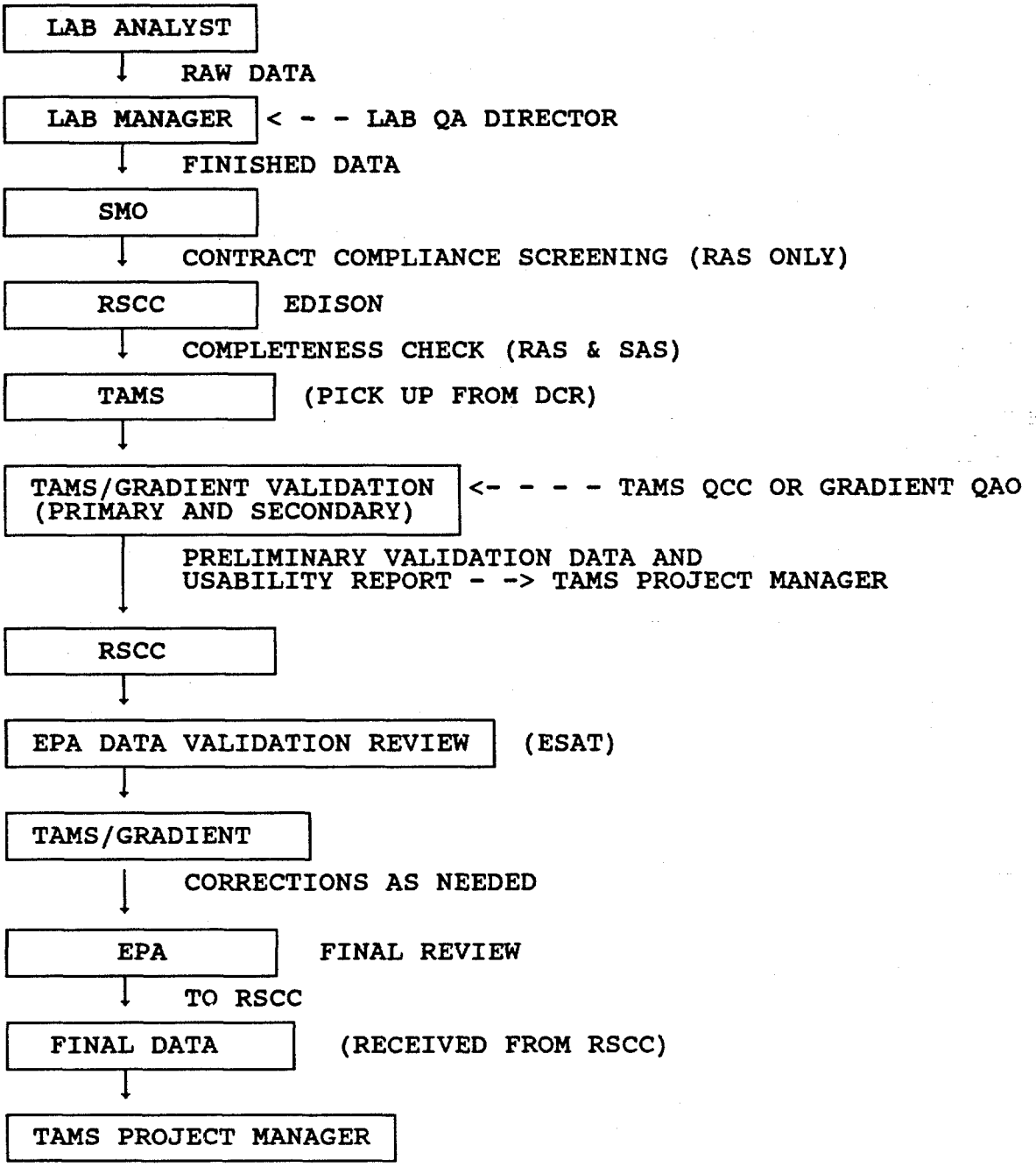
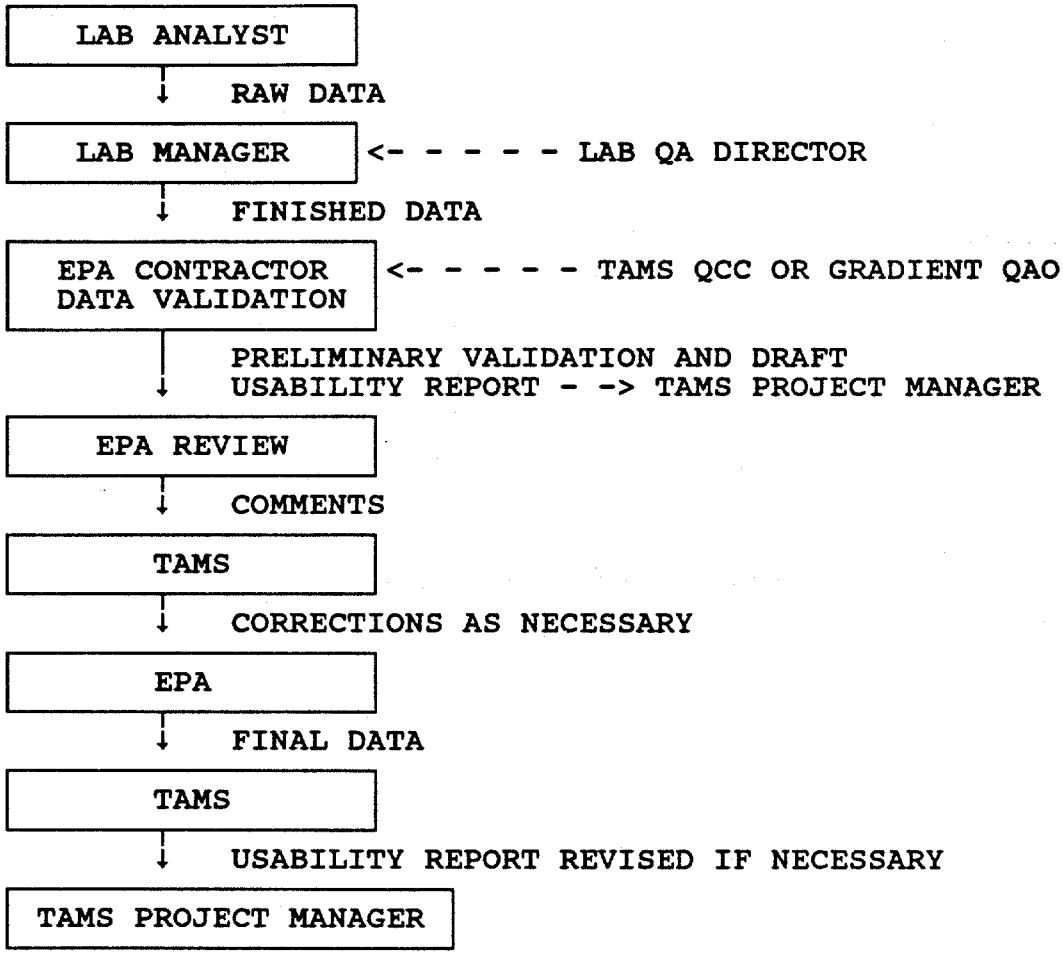


FIGURE 10-2
PROTOCOLS FOR DATA REDUCTION AND REPORTING:
LABS CONTRACTED TO TAMS



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11 Internal Quality Control Checks

The type and frequency of field, matrix, and laboratory specific Quality Control (QC) checks are summarized in Tables 11-1, 11-2, and 11-3. Method SOPs must be referenced for more detailed information (in Appendices A and B of this SAP/QAPjP).

11.1 Field Quality Control Checks

Quality control checks will be instituted as part of the sampling program. Field quality control samples to be collected include field blanks, field duplicates, and analyte-free water blanks.

11.1.1 Field Blanks

Field blanks will be collected by the field sampling team and analyzed by the laboratory in order to assess possible contamination from sampling equipment or field operations. A field blank consists of deionized analyte-free water passed through the field sampling apparatus, preserved as a sample, and submitted to the laboratory for analysis. The frequency of field blanks will be a minimum of one per decontamination event per matrix for each type of sampling equipment. Field blanks will be collected and analyzed for PCB congeners, TAL metals, and TOC. Field blanks are not specified for other analyses since the methods are not compatible with an aqueous matrix.

The analyte-free water for PCB congener field blanks will be provided by the analytical laboratory. Analyte-free water for other analyses will be procured by TAMS from a commercial source.

11.1.2 Field Duplicates

Field replicate samples (field duplicates) will be obtained to assess the adequacy (precision) of overall sampling and handling procedures. A minimum 5% frequency for field duplicate pairs (i.e., one pair per 20 samples) will be taken and analyzed per matrix per analysis. Field duplicates will be analyzed for all project parameters (PCB congeners; lipids; TAL metals, TC/TN; TIC; TOC; and grain size distribution).

11.1.3 Analyte-Free Water Blanks

The analyte-free water procured by TAMS from commercial sources is analyzed on a regular basis for TCL/TAL analytes. For the ecological investigation, analysis for TOC will also be included.

No analyte-free water blank will be submitted for PCB congener analysis. The quality of the laboratory-provided analyte-free water will be assessed by analysis of field blanks for PCB congeners and the laboratory analysis of method blanks.

11.2 Matrix Specific QC

Matrix Spike (MS)/Matrix Spike Duplicate (MSD)/Matrix Duplicate (MD) Samples: a MS/MSD pair will be performed for PCB congener analysis at the frequency of one per 20 samples (5%) per matrix or per SDG, whichever is more frequent. A MS/MD pair will be performed for TAL metals at the 5% frequency or per SDG, whichever is more frequent. All other parameters will have a matrix duplicate (MD) only. See Table 11-1 for laboratory QC summary per parameter.

The purpose of the MS is to assess matrix effects on percent recovery of the compound or analyte. MS data can also be used to measure accuracy of the method with the caution that specific matrix effects may obscure the results. MSD measures the same features as MS, with the additional information on relative percent difference (RPD) between the MS and MSD. This is a measure of the precision of the method. The MD measures precision for all analytes other than the PCB congeners in this program. The % RPD between the sample and MD concentrations are determined and compared to the criteria specified in individual SOPs and in Table 5-1. Grain-size precision is assessed by a "% similarity" criterion.

Field measurement QC checks are summarized in Table 11-2. Criteria for field measurements are given in Table 5-2.

11.3 Laboratory Quality Control Checks

Table 11-3 lists the frequency of laboratory QC checks. Accuracy and precision for LCS, MS/MSD/MD are given in Section 5. Method-specific criteria for continuing calibration checks, blanks, and other criteria are presented in the individual SOPs in the Appendices. At a minimum, the following items will be included as laboratory QC:

- Method Blanks
  These blank samples are prepared in the laboratory and are analyzed in order to assess possible laboratory contamination during the preparation or extraction procedure. The method or preparation blank must be analyzed at a frequency of one per matrix per parameter and per each batch of 20 samples or per SDG whichever is more frequent.

- Analytical Blanks
  Several inorganic methods require the routine analysis of laboratory reagent-grade water at the beginning, during and at the end of an analytical run to assess contamination and instrument drift.

The laboratory will maintain its own internal QC program, as summarized below.

- For each parameter and each matrix, minimum of one method (procedural) blank in every batch of 20 samples or SDG, whichever is more frequent, will be analyzed to detect contamination.

- For each parameter and matrix (as applicable; see Tables 11-1 and 11-3), a minimum of one laboratory control sample (LCS) per batch or every 20 samples, whichever is more frequent. The LCS will be used to access laboratory performance of the method. LCS for water samples will consist of distilled deionized water spiked with the analyte of interest. LCS (matrix spike blank) for PCB congener analysis of sediments will consist of granular sodium sulfate spiked with the same standard spike mix as used for MS Samples. Where available for other analyses, the LCS will consist of an independently prepared sample of known or accepted true

concentration (e.g., for TAL metals). However, for most analyses in this program, the ICV is equivalent to the LCS for laboratory method evaluations. For TOC and TC/TN the ICV is defined as requiring the same preparation and analysis methods as for a sample. For this reason, the ICV can be interpreted as an LCS since it fulfills the requirements of a "blank spike sample" or "laboratory control sample". For PCB congener analysis, the matrix spike blank (MSB) serves the function of the LCS.

- For PCB congeners, a minimum of one MS/MSD pair per matrix per batch of 20 samples or per SDG, whichever is more frequent, to assess accuracy and determine matrix effects.

- Surrogate standards to estimate recoveries and to account for sample-to-sample variation as required in the PCB method.

- For PCB congener analysis, 5-point multilevel initial calibrations of instruments to establish calibration curves. For other parameters, calibrations that require linear regressions to define the curve must have correlation coefficient (r) values ≥0.995. These other calibrations must consist, at a minimum, of 4 standards and one blank.

- Continuing calibration check every 5 samples for PCB congeners. For other parameters, calibration checks every 10 or 20 sample analyses (where applicable).

- Initial calibration checks or verification (ICV) performed immediately following calibration to determine accuracy of the daily calibration curve as compared to a separate source check standard. (Traceability of the ICV solution to an EPA or NBS [NIST] standard solution is recommended.)

- All PCB samples will be analyzed on a secondary capillary column for PCB congener confirmation.

- Approximately 10% of the sediment samples and 5% of the benthic invertebrate samples analyzed for PCBs will require additional confirmation by GC/ITD (Appendix A-5). The GC/ITD analyses will be performed with the same capillary columns used for the GC/ECD analyses, and will employ similar congener standard mixes. The GC/ITD analyses are intended to confirm congener identification. In addition, quantitative comparability studies between GC/ECD and GC/ITD will be conducted. Quantitative deviations in the results of the two methods should be less than 50 percent.

TABLE 11-1
LABORATORY QUALITY CONTROL SUMMARY

Laboratory Parameters	Quality Control Parameters									
	Method	ICV	ICB	CCV	CCB	LCS	MB	MS	MSD	MD
PCB congener - GC/ECD	P1			X	X	X	X	X	X	
PCB confirmation - GC/ITD	P2			X	X					
Total Organic Carbon	EPA-II	X	X	X	X	X	X			X
TC/TN	P3	X		X		X	X			X
Total Inorganic Carbon	P4	X		X		X	X			X
Metals	CLP	X	X	X	X	X	X	X		X
Grain-size	Laser									X
Lipid Content	P5						X			X

Methods:

P1 = Project specific method for PCB congeners by GC/ECD (Appendix A-4)
P2 = Project specific method for PCB congeners confirmation by GC/ITD (Appendix A-5)
P3 = Project specific method for TC/TN based on Verardo, 1990 (Appendix B-3)
P4 = Project specific method for inorganic carbon (Appendix B-4)
P5 = Project specific method for lipid determination (Appendix A-8)
EPA-II = EPA Region II Method (L. Kahn)

Notes:

In some cases, the ICV may equal the CCV or the LCS and ICB may equal CCB. See method SOP and section 11 for specific requirements. The quality control parameters are defined in Table 11-3.

TABLE 11-2
FIELD MEASUREMENT QUALITY CONTROL SUMMARY

Field Parameters	Quality Control Parameters				
	Matrix	Calibration	ICV	CCV	MD
pH	Water	X		X	X
Conductivity	Water	X			
Temperature	Water	X			
Salinity	Water	X			
Dissolved Oxygen	Water	X			X
PCB Screening	Sediment				X

Methods:

See field method SOPs in Appendix.

Notes:

pH: CCV = pH 7 buffer solution.

The quality control parameters are defined in Table 11-3.

TABLE 11-3
LABORATORY QC FREQUENCY SUMMARY

For tests that specify the following QC, this table summarizes the frequency requirements. See method SOPs and Tables 11-1 and 11-2 for applicable QC per parameter.

QC	Frequency
Initial Calibration Verification Check (ICV)	1 per analytical run immediately following calibration (all parameters except PCB congeners)
Initial Calibration Blank (ICB)	1 per analytical run immediately following the ICV where applicable (all parameters except PCB congeners)
Continuing Calibration Verification Check (CCV)	Every 12 hours during analytical run for PCB congeners (= continuing calibration check), every 10 to 20 samples for other parameters (see SOPs)
Continuing Calibration Blank (CCB)	Every 12 hours for PCB congeners. Every 10 to 20 samples immediately following CCV for other parameters where applicable (see SOPs)
Laboratory Control Sample (LCS)	1 per 20 or SDG whichever is more frequent (PCB congener analysis only LCS = matrix spike blank; other analyses the LCS may equal ICV)
Matrix Spike (MS)	1 per 20 or SDG whichever is more frequent
Matrix Spike Duplicate (MSD)	1 per 20 or SDG whichever is more frequent (PCB congener analysis only)
Matrix Duplicate (MD)	1 per 20 or SDG whichever is more frequent (all parameters expect PCB congeners)
Method (Preparation) Blank (MB)	1 per 20 or SDG whichever is more frequent
Field Blank (FB)	1 per matrix per parameter per decontamination event, where applicable
Field Duplicate (FD)	1 per matrix per parameter per 20 samples taken: minimum frequency of 5%

12 Performance and System Audits and Frequency

Audits of the field sampling team and of the laboratories performing work in support of this program will be performed under the direction of the Quality Assurance Officer. At least one field audit will be performed during sampling.

Audits during the program will be performed at a frequency to satisfy the QA Officer that the analyses are progressing within QC limits set forth in this SAP/QAPjP and following specific method SOPs documented herein. Frequency of laboratory audits may occur at biweekly intervals or greater, tapering off to monthly or quarterly as the program proceeds.

12.1 Field Audits

Specific elements of the on-site audit will include the verification of the following items:

- Completeness and accuracy of sample Chain-of-Custody (COC) forms.
- Completeness and accuracy of sample identification labels.
- Completeness and accuracy of field notebooks.
- Following proper Health & Safety procedures as outlined in the Health & Safety Plan for this project.
- Following specific decontamination procedures as outlined in Section 6.4 of this SAP/QAPjP.
- Following specific collection, preparation, preservation and storage procedures outlined in Section 6.2 and 6.3 of this SAP/QAPjP.
- Following specific calibration and analytical procedures for field parameters as outlined in field parameter SOPs in Appendices C2 through C5 of this SAP/QAPjP.
- Following handling and shipping procedures outlined in Section 6.5 and Appendix C-1 of this SAP/QAPjP.

Appendix D-1 is an example of a Field Sampling Audit Checklist.

12.2 Laboratory Audits

The TAMS-contracted laboratories involved in analyses for this program will be audited by the QA Officer or his designee at the frequency listed above. Due to the special requirements associated with many of the non-routine methods of this investigation, emphasis in these audits will focus on evaluating the technical adequacy of the analyses as it pertains to the data quality objectives. In particular, the laboratory performing the PCB congener analyses will be expected to be experienced with the methods in order to employ sound scientific judgment, as necessary.

An example checklist for laboratory audits pertaining to routine technical requirements and document control systems is provided in Appendix D-2. Items will be addressed as applicable to the specific method being reviewed during the audit. The following items, at a minimum, will be addressed:

- Sample flow through laboratory and internal sample tracking
- Chain-of-Custody
- Sample storage
- Sample preparation/extraction and analysis including:
    - SOPs
    - Logbooks or benchsheets for all preparation procedures of samples, calibration standards, QC standards/check samples, blanks
    - Logbooks or benchsheets for all analytical procedures for samples, calibrations, QC checks, matrix QC samples, blanks
    - All above documentation must include:
        - analyst initials and date
        - single-line cross-out for corrections, initials and date
        - units recorded
        - method reference number or SOP reference

- Consistency with the laboratory's QA Program Plan and the project-specific requirements of the SAP/QAPjP.

- QC samples documentation inclusive of items above and for all blanks, calibrations, calibration verification check samples, laboratory control samples, spikes, duplicates, spike duplicates, surrogates, control charts (where applicable)

- Data file storage including hard copy of all data, other media (disk, tape, etc)

- Laboratory safety procedures

- Laboratory QA procedure including internal audits, corrective action forms, QC control charts

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13 Preventive Maintenance Procedures and Schedules

Field sampling personnel will be familiar with the field calibration, operation and maintenance of the equipment, and will perform the prescribed field operating procedures outlined in the Operation and Field Manuals accompanying the respective instruments and the SOPs attached in the Appendices C-2 through C-5.

Laboratory staff will be familiar with the maintenance requirements of the instrumentation they employ. This familiarity is the result of technical education, specialized courses, and laboratory experience. Wherever possible, the laboratory will maintain a complete inventory of replacement parts needed for preventive maintenance and spare parts that routinely need replacement. It is the laboratory's responsibility to maintain maintenance log books for each instrument used in this program. These will be checked during the laboratory audits and must be kept current with information on routine and non-routine maintenance procedures.

Preventive maintenance schedules for analytical instrumentation will be specific to the laboratory's instrument manufacturer's specifications. Maintenance procedures and schedules will be outlined in the laboratory's SOPs and will be strictly adhered to for this program.

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14 Procedures Used to Assess Data Precision, Accuracy and Completeness

The following are specific definitions for precision, accuracy and completeness. Also, see Section 5 for further information.

14.1 Precision

Precision is frequently determined by the comparison of replicates, where replicates result from an original sample that has been split for identical analyses. Relative percent difference and standard deviation of a sample are commonly used in estimating precision. Percent similarity is used to assess precision of grain-size analyses.

14.1.1 Relative Percent Difference

In the case of laboratory duplicates (samples that result when an original sample has been split into two for identical analyses) or field duplicates (or co-located samples), the relative percent difference (RPD) between the two samples may be used to estimate precision.

$$RPD = \frac{D_1 - D_2}{\left(\frac{D_1 + D_2}{2}\right)} \times 100\%$$

where: D_1 = first sample value
D_2 = second sample value (duplicate or replicate)

14.1.2 Standard Deviation

Standard deviation (s) is calculated as,

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}$$

where a quantity x_i (e.g., a concentration) is measured n times with a mean $\bar{x}$.

The relative standard deviation, RSD (or sample coefficient of variation, CV), which expresses standard deviation as a percentage of the mean, is generally useful in the comparison of three or more replicates. The RSD will be used in assessing the quadruplicate TOC analyses required by the Lloyd Kahn Method.

$$RSD = 100\ (s/\bar{x})$$

or

$$CV = 100\ (s/\bar{x})$$

where: RSD = relative standard deviation, or
CV = coefficient of variation
s = standard deviation
$\bar{x}$ = mean

14.1.3 Percent Similarity

For the grain size analysis (laser method), percent similarity (Shillabeer et al., 1992) will be used rather than RPD. The Laser particle analysis divides the grain-size distribution into sixteen band sizes. Grain-size is

expressed in percentages of the sample which represent particular band sizes; these percentages make up the size distribution of the sample. Calculating the RPD for each band size of a duplicate pair does not provide an appropriate measure of precision. For example, if the distribution of the smallest band-size is 0.1% for the sample and 0.3% for the duplicate, the relative percent difference is 100%, while, in actuality, both represent a very small fraction of the entire sample. Percent Similarity (% Similarity) is the sum of the lower percents of each band size in a sample pair. For example:

Size Band	A	B	C	D		(Total)
% Sample	7	3	40	50	=	(100%)
% Duplicate	4	5	42	49	=	(100%)
Smallest %	4	3	40	49	=	96% Similarity

All analyses performed in this program will have a measure of precision in terms of matrix duplicates, matrix spike duplicates, field duplicates or in the case of some selected analyses (i.e., TOC), quadruplicates. See specific method SOPs (Appendices A and B) and Section 5 for further details.

14.2 Accuracy

The determination of accuracy of a measurement requires a knowledge of the true or accepted value for the signal being measured. Accuracy may be calculated in terms of bias as follows:

$$Bias = \bar{X} - T$$

$$\% \ Bias = \frac{100(\bar{X} - T)}{T}$$

where: $\bar{X}$ = average observed value of measurement

T = "true" value

Accuracy may also be calculated in terms of the recovery of spiked samples as in the case of matrix spike samples for this program:

$$\% \ Recovery = 100 \left[\frac{\bar{X}}{T}\right]$$

14.3 Completeness

Determining whether a data base is complete or incomplete may be quite difficult. To be considered complete, the data set must contain all QC check analyses verifying precision and accuracy for the analytical protocol. Less obvious is whether the data are sufficient to achieve the goals of the project. All data are reviewed in terms of goals in order to determine if the data base is sufficient. Following data validation, the % completeness can be obtained as the following calculation:

$$\% \ Completeness = \frac{valid \ data \ obtained}{total \ data \ planned} \ x \ 100$$

It should be noted that a number of factors may result in obtaining less than 100% of the planned data, including field conditions (e.g., a planned sampling location was inaccessible), sample handling or shipping (e.g., sample bottles broken in transit), and analytical deficiencies (serious QC problems resulting in the data being unusable [rejected]).

15 Corrective Action

The acceptance limits for the sampling and analyses to be conducted in this program have been defined in Sections 5, 8, 9 and 11. The corrective actions are likely to be immediate in nature and most often will be implemented by the field sampling personnel or laboratory analyst. The corrective action will usually involve recalculation, repreparation, reanalysis, or repetition of a sample run.

15.1 Immediate Corrective Action

Specific QC procedures and checklists are designed to help analysts detect the need for corrective action. In addition, a scientist's experience will be valuable in alerting the operator to suspicious data or malfunctioning equipment.

If a corrective action is taken as part of normal operating procedures, the collection of poor quality data will be avoided. Instrument and equipment malfunctions are amenable to this type of corrective action, and the QC procedures will include troubleshooting guides and corrective action suggestions. The actions taken will be noted in field or laboratory notebooks or benchsheets and a memorandum issued to the QA Officer within one day of the corrective action. No other formal documentation will be provided, unless further corrective action is necessary. These on-the-spot corrective actions are an everyday part of the QA/QC system. Corrective action during the field sampling portion of the program is most often a result of equipment failure or an operator oversight, and may require repeating a sampling event. Operator oversight is best avoided by having field crew members audit each other's work before and after a test. It is the responsibility of the Field Operations Leader to maintain adherence to the specified QC procedures.

Laboratory personnel will be alerted that corrective actions may be necessary if:

- QC data are outside the acceptable windows for precision and accuracy;
- Blanks contain contaminants above acceptable levels (>MDLs);
- Undesirable trends are detected in spike recoveries or the relative percent difference between duplicates;
- There are unusual changes in detection limits;

- Deficiencies are detected by the laboratory QA Director during internal audits or from the QA Officer during program audits;
- Inquiries concerning data quality are received from the client.

Corrective action procedures are often handled at the bench level by the analyst who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, and instrument sensitivity. If the problem persists or cannot be identified, the matter is referred to the Laboratory QA Manager or Director. Once resolved, full documentation of the corrective action procedure is filed with the laboratory QA department.

15.2 Long-Term Corrective Action

The need for long-term corrective action may be identified by standard QC procedures, control charts, performance, or system audits. Any quality problem which cannot be solved by immediate corrective action falls into the long-term category. The Laboratory QA Director shall see that the condition is reported to a person responsible for correcting it, who is part of a closed-loop corrective action system and follow-up plan.

The essential steps in the closed-loop corrective action system will include:

- Identification and definition of the problem.
- Delegation of responsibility for investigating the problem.
- Investigation and determination of the cause of the problem.
- Determination of a corrective action to eliminate the problem.
- Delegation and acceptance of responsibility for implementing the corrective action.
- Establishment of effectiveness of the corrective action and its implementation.
- Verification that the corrective action has eliminated the problem.

Documentation of the problem is important to the system. A Corrective Action Request Form (shown on Figure 15-1), or equivalent, will be completed by the person finding the quality problem. This form identifies the problem, possible causes and the person responsible for action on the problem. The responsible person may

be an analyst, Field Operations Leader, or the QC Director. If no person is identified as responsible for action, the QC Director will investigate the situation and determine who is responsible in each case.

The Corrective Action Request Form includes a description of the corrective action planned, the date it was taken, and space for follow-up. The QC Director will check to verify that initial action has been taken, appears effective, and at an appropriate later date will, check again to verify that the problem has been fully solved. The QC Director will receive a copy of all Corrective Action forms, and will enter them in the Corrective Action Log. This permanent record will aid the QC Director in follow-up action and this log will be reviewed by the QA officer during program audits.

Figure 15-1
Corrective Action Request Form

Corrective Action Request Form No. _____

Originator _____ Date _____
Person Responsible for Replying _____ Contract Involved _____

Description of problem and when identified: _____

State cause of problem if known or suspected: _____

Sequence of Corrective Action: (If no responsible person is identified, notify QA Manager immediately. Submit all CA forms to QA Manager for initial approval of CA.)
State Date, Person, and Action Planned:

CA Initially Approved By: _____ Date _____
Follow-up Dates: _____
Final CA Approval By: _____ Date _____

Information copies to:
RESPONSIBLE PERSON/DEPARTMENT QC COORDINATOR: _____
QA MANAGER: _____
DEPARTMENT MANAGER: _____

16 Quality Assurance Reports To Management

The Quality Assurance Officer will issue reports pertaining to all quality assurance assessments and issues which occur during the program. The reports will include, as appropriate, the results of the field and laboratory audits, document audits, significant quality problems discovered, and any necessary corrective action procedures. A data quality assessment and data usability report, based on all the samples and the data validation reports, will be incorporated into the final report.

Reports for field and laboratory audits will be submitted to the TAMS project manager within 10 days following the audit. Serious deficiencies will be reported within one day of the audit with corrective actions identified.

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18 List of Abbreviations for QA/QC Criteria

CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification (Continuing Calibration Check) Sample
CLP	Contract Laboratory Program
COC	Chain-of-Custody
DCR	Document Control Room
ESAT	Environmental Services Assistance Team (EPA Contractor)
FB	Field Blank
FD	Field Duplicate Sample
ICB	Initial Calibration Blank
ICV	Initial Calibration Verification (Initial Calibration Check) Sample
LCS	Laboratory Control Sample
MB	Method (Preparation/Extraction) Blank
MD	Matrix Duplicate Sample
MDL	Method Detection Limit
MS	Matrix Spike Sample
MSD	Matrix Spike Duplicate Sample
PARCC	Precision, Accuracy, Representativeness, Comparability, and Completeness
PE	Performance Evaluation
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPjP	Quality Assurance Project Plan
QC	Quality Control
QCC	Quality Control Coordinator
RAS	Routine Analytical Services
RPD	Relative Percent Difference
RSCC	Regional Sample Control Center
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan
SAS	Special Analytical Services

SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
TAL	Target Analyte List (Inorganics)
TCL	Target Compound List (Organics)

Appendix

A

APPENDIX A

PCB EXTRACTION, ANALYSIS, AND DATA VALIDATION

Appendix A-1
Extraction and Cleanup of Water Samples for PCB Congener Analysis

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Appendix A-1

EXTRACTION AND CLEANUP OF WATER SAMPLES FOR PCB CONGENER ANALYSIS

1.0 Scope and Application

1.1 This is a procedure for the extraction and cleanup of polychlorinated biphenyls (PCBs) from limited volume (e.g., 1-liter) aqueous samples. The procedure is based on EPA SW-846 Methods 3500A (organcic sample preparation and extraction), 3510A (separatory funnel liquid-liquid extraction), 3630 (silica gel cleanup), 3660 (sulfur cleanup), and proposed Method 3665 (concentrated sulfuric acid cleanup), with some modifications.

1.2 This extraction and cleanup procedure may be followed by congener-specific PCB analysis by gas chromatograpy/electron capture detection (GC/ECD) or GC/ion trap detector (ITD) confirmation.

2.0 Summary of Method

2.1 A measured volume of sample, approximately one liter, is solvent extracted with hexane-methylene chloride mixture in the sample bottle. The hexane-methylene chloride extract is dried with baked granular sodium sulfate and concentrated in a Kuderna-Danish (K-D) Evaporator to approximately 3 ml and cleaned using concentrated sulfuric acid.

2.2 The acid-cleaned extract is concentrated with a K-D apparatus to 1 ml, added to a silica column, and eluted with hexane to separate PCBs from chlorinated pesticides.

2.3 The eluate from the silica column cleanup is concentrated once again using a K-D apparatus and sulfur is removed using elemental mercury. The final extract volume is adjusted to 1 ml.

2.4 The final extract is suitable for gas chromatographic analysis.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware that lead to false positive peaks and/or elevated baselines in gas chromatograms. All of the reagents and glassware used must be routinely demonstrated to be free from interferences (contaminants) under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in PCB congener analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broadly eluting peaks. Common, flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of all plastics, except Teflon, in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination once it becomes a problem.

3.2 To minimize interferences from contamination, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry, dry in a 100°C oven or, if necessary, heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. (Volumetric glassware should not be heated in a muffle furnace because the calibrated volume may be affected.)

4.0 Apparatus and Materials

4.1 2-L separatory funnel
1-L graduated cylinder
100-ml graduated cylinder
250-ml Erlenmeyer flask (or equivalent)

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation Flask - 500 ml (Kontes K-5700-1-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column - Three-ball macro (Kontes K-503000-121 or equivalent).

4.2.4 Snyder column - Two-ball micro (Kontes K-569001-219 or equivalent).

4.2.5 Concentrator tube - 25 ml, graduated (Kontes 569355-0000 or equivalent).

4.2.6 Snyder column - 3 chamber (Kontes 3700560-2526 or equivalent).

4.3 Drying Column - 20 mm ID Pyrex chromatographic column with coarse frit. A small pad of disposable, hexane-washed Pyrex glass wool is substituted for the frit to help prevent cross contamination of sample extracts).

4.4 Boiling Chips - Silicon carbide or equivalent, approximately 10/40 mesh, solvent extracted with hexane for approximately one hour and heated to 400 °C for 30 minutes.

4.5 Water or steam bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a fume hood.

4.6 Vials - Amber glass 2 ml and clear glass 7 ml capacity, with Teflon lined screw caps.

4.7 Disposable glass pasteur pipette and bulb.

4.8 Balance - Analytical capable of accurately weighing ± 0.01 mg.

4.9 Apparatus for Silica Column cleanup procedure:

4.9.1 Glass chromatographic column, 11 mm ID with Teflon stopcock and reservoir.

4.9.2 50 ml beaker.

4.9.3 Long glass rod.

4.9.4 Glass wool - Rinse with methylene chloride.

4.10 Vortex mixer.

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 ASTM Type II Water (ASTM D-1193-77) or equivalent. All references to reagent water in this method refer to ASTM Type II unless otherwise specified.

5.3 Sodium sulfate (granular, anhydrous) purification is by washing with acetone/hexane followed by heating at 400 °C for four hours in a shallow tray.

5.4 Organic solvents for extraction and cleanup:

5.4.1 Acetone - Pesticide quality or equivalent.

5.4.2 Hexane - Pesticide quality or equivalent.

5.4.3 Methylene Chloride - Pesticide quality or equivalent.

5.5 Silica Gel Calibration Mix - This standard is used for the calibration of silica gel. The standard contains the compounds technical chlordane, 4,4-DDD, 4,4-DDE, 4,4-DDT, and 2,4-DDT. The purpose of this standard is to help monitor the elution pattern of analytes through the silica gel cleanup procedure.

5.6 Silicic acid (Mallinckrodt A.R. 100 mesh or equivalent) Before use, activate each batch at least 16 hours at 135°C in a shallow glass tray, loosely covered with aluminum foil. Cool to room temperature in a desiccator. Add 3.33 ml reagent water to 100 gm activated silicic acid and tumble for 4 hours.

5.6.1 Silica Gel Calibration - Prepare silica gel column as stated in section 7.12. Add 1 ml of the 30 ppb ICAL4 standard used for GC calibration and 1 ml of silica gel calibration mix (section 5.5) to a 10 ml K-D bottom and mix with a pasteur pipette. Transfer 2 ml standard to silica gel column and elute column with 30

ml hexane. Collect eluent in a 25 ml K-D tube, concentrate extract to 1.0 ml, and analyze according to congener-specific PCB method (GC/ECD).

5.6.2 Silica Gel Calibration Acceptance Criteria - All PCB congeners should have recoveries of 80-120%. The monochlorobiphenyls are the last congeners to elute through the silica gel. From the silica gel calibration mix, the extract will have a trace of alpha and gamma chlordane from the technical chlordane standard and possibly a trace of 4,4-DDD. The other pesticides 4,4-DDE, 4,4-DDT, and 2,4-DDT will have 100% recovery. This elution pattern is necessary to allow for the greatest recovery of the monochlorobiphenyls. This check should be performed every 10 days.

5.7 Mercury - 99.9% Pure (Johnson Matthey Electronics Cat. #00522)

5.8 PCB Surrogate Standard Spiking Solution

5.8.1 The surrogate standards are added to all samples, blanks, and matrix spikes prior to extraction. The surrogate compounds are tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN).

5.8.2 Prepare the surrogate standard spiking solution at a concentration of 0.2 μg/1.00 ml of each of the two compounds in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers and protect from light. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. **CAUTION**: Analysts must allow all spiking solutions to equilibrate to room temperature before use.

5.9 PCB Congener Matrix Standard Spiking Solution

5.9.1 Prepare a matrix spike standard solution that contains each of the congeners listed in Table 1 in acetone. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers and protect from light. Stock solutions must be replaced after twelve months, or sooner if comparison with check standards indicates a problem. **Caution**: Each time a vial is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration. Solutions should be stored with the smallest possible headspace,

and opening vials should be minimized. Analyst must allow all spiking solutions to equilibrate to room temperature before use.

5.9.2 Matrix spikes are also to serve as duplicates by spiking two equal aliquots from the one sample chosen for spiking.

5.10 Sodium hydroxide solution (10 N) - Dissolve 40 g NaOH (ACS reagent grade) in reagent water and dilute to 100 ml.

5.11 Sulfuric acid solution - Slowly add, with rapid stirring, 50 ml concentrated sulfuric acid (sp. gr. 1.84) to 50 ml of reagent water.

6.0 Sample Collection, Preservation, and Handling

6.1 Sample collection is according to the study protocol and relevant standard operating procedures.

6.2 Preservation - Samples will be collected and field preserved in accordance with the provisions of the SAP/QAPjP. The temperature of the shippping container must be recorded by the laboratory upon receipt. The laboratory shall note the presence of a solvent (hexane) layer in the sample bottle, if present. The laboratory shall measure and record the pH of the samples when the bottles are initially opened for extraction and analysis. In the laboratory, all samples and extracts must be protected from light and kept refrigerated at a temperature of 4° $\pm$2° C.

6.3 Holding Time - Samples must be extracted within 5 days of verified time of sample receipt (VTSR) and extracts analyzed within 40 days following VTSR.

7.0 Procedure

7.1 Samples are solvent extracted with 85:15 (v/v) hexane-methylene chloride mixture in the 1 L sample bottles.

7.2 Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide or 1:1 sulfuric acid solution. Pipet 1.0 ml of 0.2 μg/ml PCB surrogate standard spiking solution into the sample bottle and mix well. Add 1.0 ml of 0.2 μg/ml PCB congener matrix spiking solution to the designated matrix spike, matrix

spike duplicate, and matrix spike blank sample bottles. The addition of spike solutions to each sample must be witnessed by another analyst and verified on the extraction log.

7.3 Add 60 ml of 85:15 (v/v) hexane-methylene chloride mixture to sample bottle and tumble for two minutes, with periodic venting to release excess pressure. 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 volume 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 means. Transfer sample to a 2-liter separatory funnel and shake for 2 minutes. Drain sample back into tared 1-liter sample bottle and record weight of sample. Drain the hexane-methylene chloride into a 250 ml Erlenmeyer flask containing granular anhydrous sodium sulfate.

7.4 Repeat the procedure described in section 7.3 twice.

7.5 Transfer extract to a 500 ml K-D evaporation flask and attach a 10 ml concentrator tube.

7.6 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding 1.0 ml of hexane 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 hot water temperature, as required, to complete the concentration in 10 to 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 has reached 1 ml, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE K-D TUBE TO GO DRY.

7.7 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 ml of hexane.

7.8 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in the calibration solutions. Nitrogen blow-down is not recommended, since its employment may result in intermittent loss of the more volatile PCB congeners.

7.9 The extract obtained may now be cleaned with concentrated sulfuric acid. If the cleanup of the extract will not be performed immediately, transfer the concentrate, using pasteur pipet, to a 7-ml Teflon-lined screw-cap vial and store refrigerated.

7.10 Sulfuric Acid Cleanup.

7.10.1 Using a syringe or a volumetric pipette, transfer the hexane extract solution to a 7-ml vial and carefully add 3 ml of concentrated sulfuric acid. This procedure must always be done in a fume hood. CAUTION: Make sure that any exothermic reaction or evolution of gas subsides prior to proceeding.

7.10.2 Cap the vial tightly, shake for 5 seconds, and release any built-up pressure. Agitate using a vortex mixer for one minute. A vortex must be visible in the vial. CAUTION: Stop agitating immediately if the vial leaks. AVOID CONTACTING THE SOLUTION WITH BARE SKIN. SULFURIC ACID IS CAUSTIC AND WILL CAUSE SEVERE BURNS.

7.10.3 Allow the phases to separate for at least one minute. Examine the top (hexane) layer. It should not be highly colored nor should it have a visible emulsion or cloudiness. If a clean phase separation is achieved, proceed to section 7.11.4. If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial via a glass pipette and dispose of it properly. Add another 3 ml of clean sulfuric acid. NOTE: Do not remove any hexane at this stage of the procedure. Agitate the sample using a vortex mixer and allow the phases to separate as described previously.

7.10.4 Transfer the hexane layer to a clean 10 ml K-D bottom and concentrate to 1 ml.

7.11 The concentrated acid-cleaned extract may now be further cleaned on a silica column. If the clean-up of the extract will not be performed immediately, transfer the concentrate, using a pasteur pipet, to a 7-ml Teflon-lined screw-cap vial (rinsing concentrator tube with several aliquots of hexane into the vial) and store refrigerated.

7.12 Silica Gel Cleanup.

7.12.1 Silica Gel Column Preparation - Weigh 3 gm of deactivated silica gel in a 50 ml beaker and add enough methylene chloride to cover silica gel. Mix slurry to remove air bubbles. Cover beaker with aluminum foil until ready for use. Do

not let methylene chloride evaporate to expose silica gel. Place a glass wool plug at the bottom of the glass chromatographic column. Add an appropriate 10 cm equivalent volume of methylene chloride to the column and, with a glass rod, push air bubbles out of glass wool. Drain approximately 2 cm of methylene chloride to release air in stopcock. Add about 2 cm granular sodium sulfate to column. Mix with glass rod to get air bubbles out. Using the methylene chloride squirt bottle, rinse any sodium sulfate that may be stuck to sides of glass. Drain methylene chloride. DO NOT LET SODIUM SULFATE BECOME EXPOSE TO AIR.

7.12.2 Using the methylene chloride squirt bottle, rinse silica gel slurry out of the 50 ml beaker into the silica gel column. Open stopcock to let methylene chloride drain out. Rinse walls of column with methylene chloride so all of the silica get will fall into the restricted part of the column. Tap column to settle silica gel. Mark the top of silica gel with marker and continue tapping until silica gel is settled. Discard bulk of methylene chloride to 2 cm above silica gel. DO NOT LET SILICA GEL BECOME EXPOSED TO AIR.

7.12.3 Add 2 cm granular sodium sulfate to top of silica gel. Drain excess methylene chloride or use a pipette and draw off excess solvent. DO NOT LET GRANULAR SODIUM SULFATE BECOME EXPOSED TO AIR. Let the sides of the silica gel column (exposed to air) dry; then rinse sides of column with hexane and drain to top of granular sodium sulfate. Add 25 ml hexane to column and drain so that the hexane layer is just above granular sodium sulfate.

7.12.4 Extract cleanup - Transfer the 1.0 ml extract to the sorbent bed and drain to top of sodium sulfate. Rinse the 10 ml K-D bottom with 1.0 ml hexane and transfer to the silica gel column. Drain the extract to top of sodium sulfate. Start collecting the eluent at this time into K-D apparatus. Add 30 ml hexane to column and drain to the top of the sodium sulfate. Concentrate extract to approximately 1.0 ml.

7.13 If crystals of sulfur are evident or sulfur is expected to be present, the sulfur cleanup described below (section 7.14) should be performed.

7.14 Sulfur Cleanup

7.14.1 Transfer the extract from section 7.12.4 to a clear 7 ml vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1.0 ml of hexane, adding the rinsings to the 7 ml vial. If only a partial set of samples requires the cleanup for sulfur, set up a new reagent blank with 1.0 ml of hexane and take it through the mercury cleanup. Include the surrogate standards.

7.14.2 Add 1 to 2 drops of elemental mercury to the vial and cap. Agitate vial in a vortex mixer for 30 seconds.

7.14.3 If black precipitate forms, transfer extract to another vial and repeat procedure described in section 7.14.2.

NOTE: All vials containing mercury are to be handled appropriately as hazardous waste.

7.16 Final Extract Concentration - Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 ml hexane to the top. Place the K-D apparatus on a hot water or steam bath so that the concentrator tube is partially immersed 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 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.17 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of hexane. Reconnect the concentrator tube and concentrate the extract to a final volume of 1.0 ml. To ensure the final extract volume is accurate the 10 ml K-D tube must be wiped dry. Weigh the 10 ml K-D tube with the extract and boiling chips to the nearest 0.1 gram. Transfer the extract to a 2 ml amber GC vial and label as PCB fraction. Evaporate the small amount of hexane that may be left in the 10 ml K-D tube and reweigh. The final extract volume is calculated as shown below.

$$\textit{Volume (ml)} = \textit{(initial weight (g) - final weight (g))} \times \frac{1}{0.660 \textit{ (density of hexane g/ml)}}$$

The extract is ready for GC/ECD analysis. Store the extracts at 4°C (±2°C) in the dark until analyses are performed.

7.18 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in Calibration Standard #3 (see Appendix A-4). Air or nitrogen blow-down is not recommended since its employment results in intermittent loss of the more volatile PCB congeners.

8.0 Quality Control

8.1 All reagents should be checked prior to use to verify that interferences (contamination) do not exist. New solvents and other reagents should be run in a method blank prior to use on actual samples. These method blanks should be included in the GC run just prior to their intended use.

8.2 Surrogate standards must be added to all samples, matrix spike samples, blanks, and standards.

8.3 A method blank should be extracted and cleaned up with each extraction batch, each 20 samples or Sample Delivery Group, which ever is more frequent. Method blanks are extracted with the samples to monitor for any interferences introduced to the samples during preparation.

8.4 Matrix Spike and Matrix Spike Duplicate samples should be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 7-day calendar period during which samples are received, whichever is more frequent. The spiked compounds are used to monitor sample matrix effects which could interfere with the accuracy or precision of the PCB congener quantitations.

8.5 A Matrix Spike Blank should be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 7-day calendar period during which samples are received, whichever is more frequent. The spiked compounds are used to monitor the quantitative transfer of analytes through the extraction procedure unaffected by any sample matrix interferences.

8.6 The spike standard should contain the most representative compounds at a concentration appropriate to the anticipated sample concentrations (see Table 1).

9.0 References

9.1 USEPA "Test Methods for Evaluating Solid Waste" - Third Edition (SW-846) Revision 1, 1990. Methods 3500A, 3510A, 3600A, 3630A, and 3660A.

9.2 USEPA "Test Methods for Evaluating Solid Waste" - (SW-846), Proposed Update II, 1990. Method 3665.

9.3 Bopp, R.F. The geochemistry of polychlorinated biphenyls in the Hudson River. Ph.D. Dissertation, Columbia University, 1979.

9.4 NYSDEC ASP, December 1991. Method 91-11, Analytical Method for Total PCBs and PCB congeners by Fused Silica Capillary Column Gas Chromatography with Electron Capture Detector (GC/ECD).

Table 1
PCB Congener Matrix Spiking Solution

Congener	Concentration (μg/ml)
2,4'-Dichlorobiphenyl	0.2
2,2',5-Trichlorobipheny	0.2
2,4,4'-Trichlorobiphenyl	0.2
2,2',3,5'-Tetrachlorobiphenyl	0.2
2,2',5,5'-Tetrachlorobiphenyl	0.2
2,3',4,4'-Tetrachlorobiphenyl	0.2
3,3',4,4'-Tetrachlorobiphenyl	0.2
2,2',4,5,5'-Pentachlorobiphenyl	0.2
2,3,3',4,4'-Pentachlorobiphenyl	0.2
2,3',4,4',5-Pentachlorobiphenyl	0.2
3,3',4,4',5-Pentachlorobiphenyl	0.2
2,2',3,3',4,4'-Hexachlorobiphenyl	0.2
2,2',3,4,4',5'-Hexachlorobiphenyl	0.2
2,2',4,4',5,5'-Hexachlorobiphenyl	0.2
2,2',3,3',4,4',5-Heptachlorobiphenyl	0.2
2,2',3,4,4',5,5'-Heptachlorobiphenyl	0.2
2,2',3,4',5,5',6-Heptachlorobiphenyl	0.2
2,2',3,3',4,4',5,6-Octachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6-Decachlorobiphenyl	0.2

Appendix A-2
Not Applicable (Extraction and Cleanup of Large Volume Water Samples for PCB Congener Analysis)

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Appendix A-3
Extraction and Cleanup of Sediments and Particulates for PCB Congener Analysis

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Appendix A-3

EXTRACTION AND CLEANUP OF SEDIMENTS AND PARTICULATES FOR PCB CONGENER ANALYSIS

1.0 Scope and Application

1.1 This is a procedure for the extraction and cleanup of polychlorinated biphenyls (PCBs) from river sediments. The procedure is based on EPA SW-846 Methods 3500 (organic extraction and sample preparation), 3540A (soxhlet extraction), 3630A (silica gel cleanup), 3660A (sulfur cleanup), and proposed Method 3665 (concentrated sulfuric acid cleanup), with some modifications.

1.2 This extraction and cleanup procedure is appropriate for determination of congener specific PCBs by gas chromatography and electron capture detector (GC/ECD) analysis and PCB congener confirmation by GC/ITD analysis.

2.0 Summary of Method

2.1 A portion of the sediment sample or the entire particulate sample (filter) is mixed with anhydrous sodium sulfate to dryness, placed in an extraction thimble or between two plugs of glass wool, and extracted with a 50:50 (v/v) acetone/hexane solvent mixture with a soxhlet extractor. The extract is then concentrated and cleaned using concentrated sulfuric acid.

2.2 The acid-cleaned extract is added concentrated with a K-D apparatus to 1 ml, added to a silica column, and eluted with hexane to separate PCBs from chlorinated pesticides.

2.3 The eluate from the silica column cleanup is concentrated once again using a K-D apparatus and sulfur is removed using elemental mercury. The final extract volume is adjusted to 1 ml.

2.4 The final extract is suitable for gas chromatographic analysis and GC/ITD confirmation.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware that lead to false positive peaks and/or elevated baselines in gas chromatograms. All of the reagents and glassware used must be routinely demonstrated to be free from interferences (contaminants) under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in PCB congener analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broadly eluting peaks. Common, flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of all plastics, except Teflon, in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination once it becomes a problem.

3.2 To minimize interferences from contamination, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry, dry in a 100°C oven or, if necessary, heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. (Volumetric glassware should not be heated in a muffle furnace because the calibrated volume may be affected.)

4.0 Apparatus and Materials

4.1 Soxhlet Extractor - 40 mm ID, with 500-ml round bottom flask.

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation Flask - 500 ml (Kontes K-5700-1-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column - Three-ball macro (Kontes K-503000-121 or equivalent).

4.2.4 Snyder column - Two-ball micro (Kontes K-569001-219 or equivalent).

4.2.5 Concentrator tube - 25 ml, graduated (Kontes 569355-0000 or equivalent).

4.2.6 Snyder column - 3 chamber (Kontes 570050-2526 or equivalent).

4.3 Boiling Chips - Silicon carbide or equivalent, approximately 10/40 mesh, solvent extracted with hexane for approximately one hour and heated to 400°C for 30 minutes.

4.4 Water Bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a fume hood.

4.5 Vials - Amber glass 2 ml and clear glass 7 ml capacity, with Teflon lined screw.

4.6 Glass thimble or glass wool - Soxhlet extracted for at least two hours with 50:50 (v/v) acetone/hexane solvent mixture.

4.7 Heating mantle - Rheostat controlled

4.8 Disposable glass pasteur pipet and bulb.

4.9 Apparatus for determining percent dry weight.

4.9.1 Oven - Drying.

4.9.2 Desiccator.

4.9.3 Crucibles - Porcelain or disposable aluminum.

4.10 Balance - Analytical capable of accurately weighing ± 0.01 mg.

4.11 Apparatus for Silica Column cleanup procedure:

4.11.1 Glass chromatographic column, 11 mm ID with Teflon stopcock and reservoir.

4.11.2 50-mL beaker.

4.11.3 Long glass rod.

4.11.4 Glass wool - Rinsed with methylene chloride.

4.12 Vortex mixer.

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 ASTM Type II Water (ASTM D-1193-77) or equivalent. All references to reagent water in this method refer to ASTM Type II unless otherwise specified.

5.3 Sodium sulfate (granular, anhydrous) purification is by washing with acetone/hexane followed by heating at 400°C for four hours in a shallow tray.

5.4 Organic solvents for extraction and clean-up:

5.4.1 Acetone - Pesticide quality or equivalent.

5.4.2 Hexane - Pesticide quality or equivalent.

5.4.3 Methylene Chloride - Pesticide quality or equivalent.

5.5 Silica Gel Calibration Mix - This standard is used for the calibration of silica gel. The standard contains the compounds technical chlordane, 4,4-DDD, 4,4-DDE, 4,4-DDT, and 2,4-DDT. The purpose of this standard is to help monitor the elution pattern of analytes through the silica gel clean-up procedure.

5.6 Silicic acid (Mallinckrodt A.R. 100 mesh or equivalent). Before use, activate each batch at least 16 hours at 135°C in a shallow glass tray, loosely covered with aluminum foil. Cool to room temperature in a desiccator. Add 3.33-ml reagent water to 100 gm activated silicic acid and tumble for 4 hours.

5.6.1 Silica Gel Calibration - Prepare silica gel column as stated in section 7.14. Add 1 ml of the 30 ppb ICAL4 standard used for GC calibration and 1 ml of silica gel calibration mix (section 5.5) to a 10-ml K-D bottom and mix with a pasteur pipette. Transfer 2-ml standard to silica gel column and elute column with 30-ml hexane. Collect eluent in a 25-ml K-D tube, concentrate extract to 1.0 ml, and analyze according to congener-specific PCB method (GC/ECD).

5.6.2 Silica Gel Calibration Acceptance Criteria - All PCB congeners should have recoveries of 80-120%. The monochlorobiphenyls are the last congeners to elute through the silica gel. From the Silica gel calibration mix, the extract will have a trace of alpha and gamma chlordane from the technical chlordane standard and possibly a trace of 4,4-DDD. The other pesticides 4,4-DDE, 4,4-DDT, and 2,4-DDT will have 100% recovery. This elution pattern is necessary to allow for the greatest recovery of the monochlorobiphenyls. This check should be performed every 10 days.

5.7 Mercury - 99.9% Pure (Johnson Matthey Electronics Cat. #00522)

5.8 PCB Surrogate Standard Spiking Solution

5.8.1 The surrogate standards are added to all samples, blanks, and matrix spikes prior to extraction. The surrogate compounds are tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN).

5.8.2 Prepare the surrogate standard spiking solution at a concentration of 0.2 μg/1.00 ml of each of the two compounds in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers and protect from light. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. **CAUTION**: Analysts must allow all spiking solutions to equilibrate to room temperature before use.

5.9 PCB Congener Matrix Standard Spiking Solution

5.9.1 Prepare a matrix spike standard solution that contains each of the congeners listed in Table 1 in acetone. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers and protect from light. Stock solutions must be replaced after twelve months, or sooner if comparison with check standards indicates a problem.

Caution: Each time a vial is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration. Solutions should be stored with the smallest possible headspace, and opening vials should be minimized. Analyst must allow all spiking solutions to equilibrate to room temperature before use.

5.9.2 Matrix spikes are also to serve as duplicates by spiking two equal aliquots from the one sample chosen for spiking.

5.10 Sodium hydroxide solution (10 N) - Dissolve 40 g NaOH (ACS reagent grade) in reagent water and dilute to 100 ml.

5.11 Sulfuric acid solution - Slowly add, with rapid stirring, 50-ml concentrated sulfuric acid (sp. gr. 1.84) to 50-ml of reagent water.

6.0 Sample Collection, Preservation and Handling

6.1 Field sample collection, preservation, and shipping is according to the study protocol and relevant standard operating procedures as defined in the SAP/QAPjP.

6.2 Preservation - The laboratory must record the temperature of the shipping containers (coolers) upon receipt. In the laboratory, samples and extracts must be protected from light and kept refrigerated at a temperature of 4°C $\pm$ 2°C.

6.3 Holding Time - Samples must be extracted within 5 days of verified time of sample receipt (VTSR) and extracts analyzed within 40 days following VTSR.

7.0 Procedure

7.1 Sediment sample procedure

7.1.1 For sediment samples, mix sample thoroughly, especially samples which have been field composited. Discard foreign objects such as sticks, leaves, and rocks. For particulate samples, the entire filter is extracted.

7.1.2 Determination of sample % dry weight - Sediment sample results must be reported on a dry weight basis. A sample aliquot for this determination should

be weighed out at the same time as the aliquot taken for analytical determination (see 7.1.3).

7.1.3 Weigh out a 2.0 g sediment sample or place entire particulate filter for extraction into a tared 50-ml beaker. Immediately after weighing the sediment sample for extraction, weigh another aliquot (1 - 2 g), weight to nearest 0.001 g accuracy of the sample into a tared crucible or aluminum weighing dish. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

% dry weight = (g dry sample/g sample) x 100%

7.1.4 Blend 2 g of sediment with 2 g anhydrous sodium sulfate (the sodium sulfate should be added in small aliquots). Place in a pre-cleaned extraction thimble. The thimble and glass wool should be soxhlet extracted for approximately six cycles prior to using. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of 0.2 μg/mL surrogate standard spiking solution onto the sample. For the sample in each analytical batch selected for spiking, add 1.0 ml of 0.2 μg/mL matrix spike standard solution. The surrogate and matrix spiking procedures must be witnessed by another analyst, and verified on the extraction log. Proceed to step 7.3.

7.2 Filtered Particulate sample procedure

7.2.1 For filtered particulate samples, blend the entire filter with 2 g anhydrous sodium sulfate (the sodium sulfate should be added in small aliquots) in the extractor. A small amount of water, equal to the weight of the filter, must be added to filtered particulate samples prior to extraction. Place in a pre-cleaned extraction thimble. The thimble and glass wool should be soxhlet extracted for approximately six cycles prior to using. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of 0.2 μg/mL surrogate standard spiking solution onto the sample. For the sample in each analytical batch selected for spiking, add 1.0 ml of 0.2 μg/mL matrix spike standard solution. The surrogate and matrix spiking procedures must be witnessed by another analyst, and verified on the extraction log.

7.2.2 Proceed to step 7.3.

7.3 Place 300 ml 50:50 (v/v) of acetone/hexane solvent mixture into a 500-ml round bottom flask containing one or two clean boiling chips (rinse 50-ml beaker with 100 of the 300 ml). Attach the flask to the extractor and extract the sample for approximately 16 hours at 4 - 6 cycles/hr.

7.4 Allow the extract to cool after the extraction is complete.

7.5 Assemble a K-D concentrator by attaching a 10-ml concentrator tube to a 500-ml evaporation flask.

7.6 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding 1.0 ml of hexane 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 hot 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 has reached 1-2 ml, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE K-D TUBE TO GO DRY.

7.7 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 ml of hexane.

7.8 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in the calibration solutions. Nitrogen blow-down is not permitted, since its employment may result in intermittent loss of the more volatile PCB congeners.

7.9 The extracts obtained may now be cleaned with concentrated sulfuric acid. If the clean-up of the extract will not be performed immediately, transfer the concentrate, using a pasteur pipet, to a 7-ml Teflon-lined, screw-cap vial (rinsing concentrator tube with several aliquots of hexane into the vial) and store refrigerated.

7.10 Sulfuric Acid Cleanup.

7.10.1 Using a syringe or a volumetric pipette, transfer the hexane extract solution to a 7-ml vial and carefully add 3 ml of concentrated sulfuric acid. This procedure must always be done in a fume hood. CAUTION: Make sure that any exothermic reaction or evolution of gas subsides prior to proceeding.

7.10.2 Cap the vial tightly, shake for 5 seconds, and release any built-up pressure. Agitate using a vortex mixer for one minute. A vortex must be visible in the vial. CAUTION: Stop agitating immediately if the vial leaks. AVOID CONTACTING THE SOLUTION WITH BARE SKIN. SULFURIC ACID IS CAUSTIC AND WILL CAUSE SEVERE BURNS.

7.10.3 Allow the phases to separate for at least one minute. Examine the top (hexane) layer. It should not be highly colored nor should it have a visible emulsion or cloudiness. If a clean phase separation is achieved, proceed to section 7.12.4. If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial via a glass pipette and dispose of it properly. Add another 3 ml of clean sulfuric acid. NOTE: Do not remove any hexane at this stage of the procedure. Agitate the sample using a vortex mixer and allow the phases to separate as described previously.

7.10.4 Transfer the hexane layer to a clean 10-ml K-D bottom and concentrate to 1 ml.

7.11 The concentrated acid-cleaned extract may now be further cleaned on a silica column. If the clean-up of the extract will not be performed immediately, transfer the concentrate, using a pasteur pipet, to a 7 ml Teflon-lined, screw-cap vial (rinsing concentrator tube with several aliquots of hexane into the vial) and store refrigerated.

7.12 Silica Gel Cleanup.

7.12.1 Silica Gel Column Preparation - Weigh 3 gm of deactivated silica gel in a 50-ml beaker and add enough methylene chloride to cover silica gel. Mix slurry to remove air bubbles. Cover beaker with aluminum foil until ready for use. Do not let methylene chloride evaporate to expose silica gel. Place a glass wool plug at the bottom of the glass chromatographic column. Add an appropriate 10 cm equivalent volume of methylene chloride to the column and, with a glass rod, push air bubbles out of glass wool. Drain approximately 2 cm of methylene

chloride to release air in stopcock. Add about 2-cm granular sodium sulfate to column. Mix with glass rod to get air bubbles out. Using the methylene chloride squirt bottle, rinse any sodium sulfate that may be stuck to sides of glass. Drain methylene chloride. DO NOT LET SODIUM SULFATE BECOME EXPOSE TO AIR.

7.12.2 Using the methylene chloride squirt bottle, rinse silica gel slurry out of the 50-ml beaker into the silica gel column. Open stopcock to let methylene chloride drain out. Rinse walls of column with methylene chloride so all of the silica get will fall into the restricted part of the column. Tap column to settle silica gel. Mark the top of silica gel with marker and continue tapping until silica gel is settled. Discard bulk of methylene chloride to 2-cm above silica gel. DO NOT LET SILICA GEL BECOME EXPOSED TO AIR.

7.12.3 Add 2-cm granular sodium sulfate to top of silica gel. Drain excess methylene chloride or use a pipette and draw off excess solvent. DO NOT LET GRANULAR SODIUM SULFATE BECOME EXPOSED TO AIR. Let sides of silica gel column (exposed to air) dry; then rinse sides of column with hexane and drain to top of granular sodium sulfate. Add 25-mls hexane to column and drain so hexane layer is just above granular sodium sulfate.

7.12.4 Extract cleanup - Transfer the 1.0-ml extract to the sorbent bed and drain to top of sodium sulfate. Rinse the 10-ml K-D bottom with 1.0-ml hexane and transfer to the silica gel column. Drain the extract to top of sodium sulfate. Start collecting the eluent at this time into K-D apparatus. Add 30-ml hexane to column and drain to top of sodium sulfate. Concentrate extract to approximately 1.0 ml.

7.13 If crystals of sulfur are evident or sulfur is expected to be present, the sulfur cleanup described below (section 7.14) should be performed.

7.14 Sulfur Cleanup

7.14.1 Transfer the extract from section 7.14.4 to a clear 7-ml vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1.0 ml of hexane, adding the rinsings to the 7-ml vial. If only a partial set of samples requires the cleanup for sulfur, set up a new reagent blank with 1.0 ml of hexane and take it through the mercury cleanup. Include the surrogate standards.

7.14.2 Add 1-2 drops of elemental mercury to the vial and cap. Agitate vial in a vortex mixer for 30 seconds.

7.14.3 If black precipitate forms, transfer extract to another vial and repeat procedure described in section 7.14.2.

NOTE: All vials containing mercury are to be handled appropriately as hazardous waste.

7.15 Final Extract Concentration - Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1-ml hexane to the top. Place the K-D apparatus on a hot water or steam bath so that the concentrator tube is partially immersed 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 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.16 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of hexane. Reconnect the concentrator tube and concentrate the extract to a final volume of 1.0 ml. To obtain an accurate final extract volume, the 10-ml K-D tube must be wiped dry. Weigh the 10-ml K-D tube with the extract and boiling chips to the nearest 0.1 gram. Transfer the extract to a 2-ml amber GC vial and label as PCB fraction. Evaporate the small amount of hexane that may be left in the 10-ml K-D tube and reweigh. The final extract volume is calculated as shown below.

$$\textit{Volume (ml)} = \textit{(initial weight (g) - final weight (g))} \times \frac{1}{\textit{0.660 (density of hexane g/ml)}}$$

The extract is ready for GC/ECD analysis. Store the extracts at 4°C (±2°C) in the dark until analyses are performed.

7.17 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in Calibration Standard #3 (see Appendix A-4). Air or nitrogen blow-down is not permitted since its employment results in intermittent loss of the more volatile PCB congeners.

8.0 Quality Control

8.1 All reagents should be checked prior to use to verify that interferences (contamination) do not exist. New solvents and other reagents should be run in a method blank prior to use on actual samples. These method blanks should be included in the GC run just prior to their intended use in the PCB congener extraction procedure.

8.2 Surrogate standards should be added to all samples, matrix spike samples, blanks, and standards.

8.3 A method blank should be extracted and cleaned-up with every extraction batch, each 20 samples, or Sample Delivery Group, which ever is more frequent. Method blanks are extracted with the samples to monitor for any interferences (contamination) introduced to the samples during preparation.

8.4 Matrix Spike and Matrix Spike Duplicate samples should be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 7-day calendar period during which samples are received, whichever is more frequent. The spiked compounds are used to monitor sample matrix effects which could interfere with the accuracy or precision of the PCB congener quantitations.

8.5 A Matrix Spike Blank should be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 7-day calendar period during which samples are received, whichever is more frequent. The spiked compounds are used to monitor the quantitative transfer of analytes through the extraction procedure, unaffected by any sample matrix interferences.

8.6 The spike standard should contain the most representative compounds at a concentration appropriate to the anticipated sample concentrations (see Table 1).

9.0 References

9.1 USEPA "Test Methods for Evaluating Solid Waste" - Third Edition (SW-846) Revision 1, 1990. Methods 3500A, 3540A, 3600A, 3630A, and 3660A.

9.2 USEPA "Test Methods for Evaluating Solid Waste" (SW-846), Proposed Update II, 1990. Method 3665.

9.2 Bopp, R.F. The geochemistry of polychlorinated biphenyls in the Hudson River. Ph.D. Dissertation, Columbia University, 1979.

Table 1
PCB Congener Matrix Spiking Solution

Congener	Concentration (μg/mL)
2,4'-Dichlorobiphenyl	0.2
2,2',5-Trichlorobipheny	0.2
2,4,4'-Trichlorobiphenyl	0.2
2,2',3,5'-Tetrachlorobiphenyl	0.2
2,2',5,5'-Tetrachlorobiphenyl	0.2
2,3',4,4'-Tetrachlorobiphenyl	0.2
3,3',4,4'-Tetrachlorobiphenyl	0.2
2,2',4,5,5'-Pentachlorobiphenyl	0.2
2,3,3',4,4'-Pentachlorobiphenyl	0.2
2,3',4,4',5-Pentachlorobiphenyl	0.2
3,3',4,4',5-Pentachlorobiphenyl	0.2
2,2',3,3',4,4'-Hexachlorobiphenyl	0.2
2,2',3,4,4',5'-Hexachlorobiphenyl	0.2
2,2',4,4',5,5'-Hexachlorobiphenyl	0.2
2,2',3,3',4,4',5-Heptachlorobiphenyl	0.2
2,2',3,4,4',5,5'-Heptachlorobiphenyl	0.2
2,2',3,4',5,5',6-Heptachlorobiphenyl	0.2
2,2',3,3',4,4',5,6-Octachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	0.2

Appendix A-4
Congener Specific Determination of Polychlorinated Biphenyls (PCBs) in Hexane Extracts by Capillary Column Gas Chromatography

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Appendix A-4

CONGENER SPECIFIC DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) IN HEXANE EXTRACTS BY CAPILLARY COLUMN GAS CHROMATOGRAPHY

1.0 Scope and Application

1.1 This method describes procedures for the calibration, analysis, and quantitation of 90 of the possible 209 polychlorinated biphenyl (PCB) congeners by fused silica capillary column gas chromatography with electron capture detection (GC/ECD). The method is applicable to samples, extracted in hexane, containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. Ninety PCBs are identified and quantitated by congener. For other PCB congeners for which calibration is not performed, a qualitative identification is based on historical relative retention time information and quantitation is made using the response factor for BZ#52. Samples must be extracted and applicable cleanup procedures performed prior to analysis by GC/ECD.

2.0 Summary of Method

2.1 Hexane extracts are analyzed for PCB congeners on a fused silica capillary column gas chromatograph with an electron capture detector (GC/ECD). PCB congeners are identified using two capillary columns of different polarity in parallel. Prior to sample analysis, the laboratory is required to use individual congener standards to determine the retention time order of the resolvable congener peaks for each column that is used in the analysis. The laboratory will also determine the method detection limit for each of the resolvable PCB congener peaks. A five-point calibration, using the individual PCB congeners listed in Table 1, will be performed for quantitation. Instrument stability will be verified every 12 hours with a mid-level standard.

2.2 Method interferences may be caused by septa bleed, contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials will be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory instrument and method blanks.

Sample matrix interferences are also a concern, therefore three sample extract cleanups - sulfuric acid, silica gel, and sulfur cleanup (see appropriate matrix-specific SOPs for extraction and cleanup protocols) - are the minimum sample preparation techniques which will be employed.

3.0 Apparatus and Materials

3.1 Gas chromatograph - Hewlett Packard 5890 series II gas chromatograph analytical system with dual capillary columns, dual detectors, packed column or on-column injection, and required accessories including syringes, gases, electron capture detectors, strip-chart recorder with recording integrator, and auto-sampler, or equivalent.

3.2 Fused Silica Capillary Columns

- Column 1 - 50 m x 0.22 mm ID, 0.25 micron film thickness, SB-Octyl-50, DIONEX
- Column 2 - 60 m x 0.25 mm ID, 0.25 micron film thickness, RTX-5, Restek Corp.
- Column 3 - 50 m x 0.20 mm ID, 0.33 micron film thickness HP-5, Hewlett Packard

3.3 A data system capable of handling a minimum of 120 chromatographic peaks per detector is required for measuring peak areas or peak heights, recording retention times, and calculating data. Fison's Multi-Chrom version 2.0, or equivalent, is recommended.

3.4 Analytical balance capable of accurately weighing ± 0.01 mg.

4.0 Reagents

4.1 Solvents

Hexane - Pesticide quality or equivalent. (J.T. Baker, Resi-Analyzed, is recommended.)
Acetone - Pesticide quality or equivalent. (J.T. Baker, Resi-Analyzed, is recommended.)
Toluene - Pesticide quality or equivalent.

4.2 Stock Standard Solutions. Stock standards of each of the PCB congeners listed in Table 1, and any additional individual PCB congeners that the laboratory has identified to be resolvable and commercially available, are purchased from vendors as individual standards at the highest concentration available. Stock solutions should be at concentrations high enough to meet the concentration of the highest level calibration standard when combined into calibration mixtures (refer to section 4.4). Place stock standard solutions in clean glass vials with Teflon-lined screw caps and store at 4°C (±2°C), protected from light. The stock solution must be replaced after twelve months, or sooner, if comparison with check standards indicates a problem.

4.3 Primary Dilution Standard Solutions. Individual stock standards are combined to make six intermediate stock solutions called the Primary Dilution Standard Solutions. If additional compounds are needed, a seventh standard solution will be used until new standards are formulated.

4.4 Calibration Standard Solutions. Calibration standards are prepared by diluting Primary Dilution Standard Solutions (section 4.3) with hexane. Five concentration levels, such that Calibration Standard #1 contains each of the appropriate PCB congeners at a concentration roughly 5 times the MDL for that congener, are prepared. Tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN) surrogates will be spiked into each standard (see accompanying SOPs for extraction of PCBs from sediment and water, Appendices A-1 through A-3). Place each calibration standard solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C (±2°C) protected from light. Initial calibration (ICAL) and continuing calibration (OCAL) standard solutions should be defined as follows:

ICAL1 All PCB congeners are at a 1.0 µg/l concentration except the monochlorobiphenyls which are at 5.0 µg/l. The surrogates TCMX and OCN are at a 3.0 µg/l concentration.

ICAL2 All PCB congeners are at a 3.0 µg/l concentration except the monochlorobiphenyls which are at 15.0 µg/l. The surrogates TCMX and OCN are at 9.0 µg/l concentration.

ICAL3 All PCB congeners are at a 10 µg/l concentration except the monochlorobiphenyls which are at 50 µg/l. The surrogates TCMX and OCN are at 30 µg/l concentration.

ICAL4 All PCB congeners are at a 30 µg/l concentration except the monochlorobiphenyls which are at 150 µg/l. The surrogates TCMX and OCN are at a 90 µg/l concentration.

ICAL5 All PCB congeners are at a 100 µg/l concentration except the monochlorobiphenyls which are at 500 µg/l. The surrogates TCMX and OCN are at a 300 µg/l concentration.

OCAL3 All PCB congeners are at a 10 µg/l concentration except the monochlorobiphenyls which are at 50 µg/l. The surrogates TCMX and OCN are at 30 µg/l concentration.

5.0 Calibration

5.1 Initial Calibration.

The gas chromatographic system must initially be calibrated using the external standard technique for all columns used for quantitation. Tables 2A and 2B provide operating conditions for gas chromatography.

Both capillary columns will be used to quantify individual PCB congeners; therefore, both columns must meet the following quality control criteria for calibration.

5.1.1 The initial calibration sequence from the point of injection is as follows:

1. Instrument Blank
2. ICAL1
3. ICAL2
4. ICAL3
5. ICAL4
6. ICAL5
7. Instrument Blank

5.1.2 Resolution Criteria - The ICAL3 standard is used to measure the resolution of peaks.

SB-Octyl-50 - Should have greater than 50% resolution for the following pairs of PCB congeners:

1. BZ#5 and BZ#8
2. BZ#41 and BZ#40
3. BZ#183 and BZ#185
4. BZ#209 and Octachloronaphthalene

HP-5 - Should meet the resolution criteria for the following pair of PCB congeners:

1. BZ#4 and BZ#10, which coelute, and TCMX should have greater than 25% resolution.

2. BZ#31 and BZ#28 should have greater than 25% resolution.

3. BZ#84 and BZ#101 should have greater than 50% resolution

4. BZ#206 and OCN should have greater than 50% resolution.

5.1.3 Calculation for Resolution

$$Resolution = \frac{height\ of\ smaller\ peak - height\ of\ valley}{height\ of\ smaller\ peak} \times 100$$

The height of the smaller peak and valley can be measured with a millimeter ruler, to the closest 0.5 millimeter.

5.1.4 Linearity

The linearity of each PCB congener is assessed using a quadratic weighted least squares regression model generated from the five point calibration. The following quality control criteria must be met on both analytical columns:

5.1.4.1 The Percent Relative Standard Concentration Error (%RSCE) using all five calibration points must be less than 15% with the exception of the monochlorobiphenyls and any two other PCB congeners which must be less than 20%

% RSCE = SD (n-1) of the % conc. error from the 5-pt calibration

$$\% \ Conc.\ error = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100$$

where:

SD = standard deviation

n = number of calibration points

conc. = concentration

C_{calc} = calculated concentration

C_{nom} = nominal (true) concentration

5.1.4.2 The correlation coefficient of the five calibration points must be ≥ 0.995 using the quadratic equation with 1/x weighting, where x equals concentration.

5.1.5 Retention Time Criteria

Each compound in the curve must fall within the specified retention time windows using the mean retention time of the five calibration points. The retention time windows are ± 0.25 for the monochlorobiphenyls, dichlorobiphenyls, trichlorobiphenyls, tetrachlorobiphenyls, and tetrachloro-m-xylene, and ± 0.35 for the remaining PCB congeners and OCN.

5.1.6 Instrument blanks must not have any analytes detected above the calibrated quantitation limit (CQL, equivalent to concentration of the lowest calibration standard).

5.2 Continuing Calibration

The continuing calibration standard (OCAL3) must be analyzed every 12 hours and must meet the following quality control criteria. If the quality control criteria are not met, samples analyzed between the last passing standard and the failing standard must be re-analyzed.

5.2.1 The typical run sequence beginning with the initial calibration is as follows:

1 through 5.	Instrument Blank and ICAL standards (see section 5.1)	
6.	ICAL5	(0 hour for first analytical window)
7.	Instrument Blank	
8.	Samples	
9.	Instrument Blank	(first injection after 12 hours)
10.	OCAL3	(0 hour for second analytical window)
11.	Samples	
12.	Instrument Blank	(first injection after 12 hours)
13.	OCAL3	(0 hour for third analytical windows)

5.2.2 The percent difference (%D) of the calculated concentration for the OCAL3 must be less than ±20% compared to the nominal (true) concentration, with the exception of the monochlorobiphenyls and any two other PCB congeners which must be less than ±25%.

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100\%$$

where:

C_{calc} = calculated concentration

C_{nom} = nominal (true) concentration

5.2.3 The retention times of each PCB congener must fall within the required retention time windows discussed in Section 5.1.5.

5.2.4 The resolution criteria stated in Section 5.1.3 should be met to continue the analysis.

6.0 Method Detection Limit (MDL) and Extraction Efficiency Determinations

Prior to receiving environmental samples, the laboratory must determine method detection limits for the suite of PCB congener matrix spiking compounds identified in the accompanying SOPs for the extraction and clean-up of sediment and water samples (Appendices A-1 through A-3). The laboratory must also demonstrate that acceptable PCB congener extraction efficiencies can be obtained using the extraction and analysis procedures defined in this and the accompanying SOPs.

6.1 MDL Determination for 1 Liter Water Samples

6.1.1 Prepare seven low level PCB congener MDL standards by spiking seven one-liter volumes of reagent water with 3 to 5 times the concentration of the required detection limit for each congener (see SOP "Extraction and Clean-Up of Water Samples for PCB Congener Analyses").

6.1.2 Extract these low level PCB MDL standards following the procedures outlined in the SOP "Extraction and Cleanup of Water Samples for PCB Congener Analyses").

6.1.3 Analyze the low level PCB MDL standards as described in Section 7 herein.

6.1.4 Calculate the standard deviation of the results for each congener for the seven analyses as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x}_i)^2}{N - 1}}$$

where,

SD = Standard Deviation of the results for each congener

x_i = mean result time for congener(i)

N = 7 (number of MDL standard results)

6.1.5 Calculate the MDL for each congener as follows:

MDL = 3.14 x SD

6.2 MDL Determination for 16-Liter Water Samples

6.2.1 Prepare seven low level PCB congener MDL standards by spiking 3 to 5 times the concentration of the required detection limit for each congener into each of seven 16-liter volumes of reagent water. Each 16-liter volume of spiked solution is derived from 5 spiked 3.2 liter volumes, the extracts of which are combined.

6.2.2 Extract these low level PCB MDL standards following the procedures outlined in the SOP "Extraction and Cleanup of Large Volume Water Samples for PCB Congener Analyses".

6.2.3 Repeat steps 6.1.3 to 6.1.5.

6.3 MDL Determination for Sediment Samples

6.3.1 Prepare seven low level PCB congener MDL standards by spiking 3 to 5 times the concentration of the required detection limit for each congener into each of seven 2-gram samples of EPA-certified clean sand.

6.3.2 Extract these low level PCB MDL standards following the procedures outlined in the SOP "Extraction and Cleanup of Sediment Samples for PCB Congener Analyses".

6.2.3 Repeat steps 6.1.3 to 6.1.5.

6.4 Extraction Efficiency Determinations

6.4.1 Extraction efficiency determinations will be evaluated on four environmental samples for each matrix of interest, which are supplied to the laboratory.

6.4.2 The laboratory must extract and analyze each sample according to this and appropriate matrix-specific SOPs.

6.4.3 The laboratory must save the extracted samples and then re-extract those samples using the same procedures as specified in 6.4.2.

4.2 Stock Standard Solutions. Stock standards of each of the PCB congeners listed in Table 1, and any additional individual PCB congeners that the laboratory has identified to be resolvable and commercially available, are purchased from vendors as individual standards at the highest concentration available. Stock solutions should be at concentrations high enough to meet the concentration of the highest level calibration standard when combined into calibration mixtures (refer to section 4.4). Place stock standard solutions in clean glass vials with Teflon-lined screw caps and store at 4°C (±2°C), protected from light. The stock solution must be replaced after twelve months, or sooner, if comparison with check standards indicates a problem.

4.3 Primary Dilution Standard Solutions. Individual stock standards are combined to make six intermediate stock solutions called the Primary Dilution Standard Solutions. If additional compounds are needed, a seventh standard solution will be used until new standards are formulated.

4.4 Calibration Standard Solutions. Calibration standards are prepared by diluting Primary Dilution Standard Solutions (section 4.3) with hexane. Five concentration levels, such that Calibration Standard #1 contains each of the appropriate PCB congeners at a concentration roughly 5 times the MDL for that congener, are prepared. Tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN) surrogates will be spiked into each standard (see accompanying SOPs for extraction of PCBs from sediment and water, Appendices A-1 through A-3). Place each calibration standard solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C (±2°C) protected from light. Initial calibration (ICAL) and continuing calibration (OCAL) standard solutions should be defined as follows:

ICAL1 All PCB congeners are at a 1.0 µg/l concentration except the monochlorobiphenyls which are at 5.0 µg/l. The surrogates TCMX and OCN are at a 3.0 µg/l concentration.

ICAL2 All PCB congeners are at a 3.0 µg/l concentration except the monochlorobiphenyls which are at 15.0 µg/l. The surrogates TCMX and OCN are at 9.0 µg/l concentration.

ICAL3 All PCB congeners are at a 10 µg/l concentration except the monochlorobiphenyls which are at 50 µg/l. The surrogates TCMX and OCN are at 30 µg/l concentration.

ICAL4 All PCB congeners are at a 30 µg/l concentration except the monochlorobiphenyls which are at 150 µg/l. The surrogates TCMX and OCN are at a 90 µg/l concentration.

ICAL5 All PCB congeners are at a 100 µg/l concentration except the monochlorobiphenyls which are at 500 µg/l. The surrogates TCMX and OCN are at a 300 µg/l concentration.

OCAL3 All PCB congeners are at a 10 µg/l concentration except the monochlorobiphenyls which are at 50 µg/l. The surrogates TCMX and OCN are at 30 µg/l concentration.

5.0 Calibration

5.1 Initial Calibration.

The gas chromatographic system must initially be calibrated using the external standard technique for all columns used for quantitation. Tables 2A and 2B provide operating conditions for gas chromatography.

Both capillary columns will be used to quantify individual PCB congeners; therefore, both columns must meet the following quality control criteria for calibration.

5.1.1 The initial calibration sequence from the point of injection is as follows:

1. Instrument Blank
2. ICAL1
3. ICAL2
4. ICAL3
5. ICAL4
6. ICAL5
7. Instrument Blank

6.4.4 Extraction efficiencies will be evaluated as the mass of congener removed in the first extraction divided by the sum of the masses of congener removed in the first and second extractions, as follows:

$$EE = \frac{M_f}{M_f + M_s} \times 100\%$$

Where:

EE = extraction efficiency

M_f = mass of congener removed in first extraction

M_s = mass of congener removed in second extraction

6.4.5 Extraction efficiencies must be calculated for each congener and for each sample analyzed. Extraction efficiencies must be at least 95%. If any extraction efficiency for any congener is below 95%, the laboratory must contact the Quality Assurance Officer for the project to review the analyses and decide upon corrective action.

7.0 GC/ECD Primary Analysis

7.1 Quantitation will be performed on primary and confirmation analyses.

7.2 Sample analysis of extracts can begin when QA/QC requirements specified in Section 5.1 have been met.

7.3 After the analysis of each group of samples, analyze an instrument blank followed by OCAL3. The PCB analytical sequence must end with OCAL3 regardless of the number of samples analyzed.

7.4 If the samples are split between two or more instruments, the complete set of standards must be analyzed on each instrument with the same calibration requirements. All standards must be analyzed prior to the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

7.5 Paragraphs 7.7 and 7.8 contain GC performance criteria. If it is determined during the course of the analytical sequence that one or more of the criteria have been violated, stop the run and take corrective action. After corrective action has been taken, the analytical sequence may be restarted as follows.

7.4.1 If a standard violated the criterion, restart the sequence with the previous standard, determine that the criteria have been met and continue with sample analyses, according to 7.9.1.

7.4.2 If a sample violated the criterion, restart the sequence with the standard that preceded that group of samples (thereby preserving the sequence of standards in 7.9.1), determine that the criteria have been met and continue with sample analysis, according to 7.9.1.

7.6 If it is determined after completion of an analytical run that one or more criterion have been violated, proceed as follows.

7.6.1 If a standard violated the criterion, all samples analyzed after the previous compliant standard must be re-analyzed as part of a new analytical sequence.

7.6.2 Following the non-compliant standard, a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard previous to the standard that did not meet the criterion and the compliant standard must be re-analyzed as part of a new analytical sequence.

7.6.3 If only samples violated the criterion, then those samples must be re-analyzed as part of a new analytical sequence.

7.7 The percent difference (%D) of the nominal (true) concentration as compared to the calculated concentration for each congener in the continuing calibration standard (OCAL3) must be less than $\pm 20\%$.

7.8 The retention time shift of the TCMX and OCN surrogates in any standard or sample must be less than ± 0.25 and ± 0.35 minutes, respectively, from the mean retention time determined from the initial calibration.

7.9 Inject the sample or standard extract using either the solvent-flush technique or an auto sampler. Smaller volumes can be injected only if automatic devices are employed. Record both the volume injected (to the nearest 0.05 μl) and the total extract volume.

7.9.1 The analytical sequence must be as follows:

1. Instrument Blank
2. ICAL1
3. ICAL2
4. ICAL3
5. ICAL4
6. ICAL5 (0 hour for first analytical window)
7. Instrument Blank
8. Samples
9. Instrument Blank (first injection after 12 hours)
10. OCAL3 (0 hour for second analytical window)
11. Samples
12. Instrument Blank (first injection after 12 hours)
13. Repeat the above sequence starting with OCAL3 (step 10 above)
14. PCB congener analysis sequence must end with the analyses of OCAL3

7.9.2 Analyze the method blank (extracted with each set of samples) on each GC on which samples are analyzed.

7.10 Evaluate the Primary Analysis chromatograms according to the following guidance.

7.10.1 Consider the sample nondetect when all PCB congener peaks result in concentrations less than 0.1 ng/ml in extract for all PCB congeners (0.5 mg/ml in extract for monochlorobiphenyls). The sample analysis is complete at this point. Confirmation is not required.

7.10.2 Tentative identification is when a compound(s) retention time falls within the retention time window calculated from the initial calibration mean retention time.

7.10.3 Determine if any PCB congeners are present based upon the following criteria:

- If the response for all compounds is less than or equal to two times the response of the highest concentration calibration standard the extract is ready for confirmation and quantitation.

- If the response for any compound is greater than two times the response for the highest concentration calibration standard, dilute the extract so

that the peak will be approximately midway in the calibration range and re-analyze. Use this same dilution for confirmation and quantitation.

7.10.4 If identification of compounds of interest are prevented by the presence of interferences, further cleanup may be required.

7.10.5 When selecting a GC column for confirmation and/or quantitation, be sure as few as possible of the PCB congeners to be confirmed/quantitated overlap. When samples are very complex, it may be necessary to use more than two columns to achieve adequate separation (>75% resolution) for as many PCB congeners as possible for accurate quantitation. Recommended capillary columns are listed in Section 3.2. The analyst should be aware that coeluting PCB congeners on one column may coelute with different PCB congeners on a different column.

8.0 GC/ECD Confirmation Analysis

8.1 Confirmation Analysis is performed to confirm the identification and quantification of all PCB congeners tentatively identified in the Primary Analysis. Since the method analyzes sample extracts simultaneously on two parallel chromatography columns, each with its own detector, the Confirmation Analysis is performed at the same time as the Primary Analysis. All Primary Analysis QA/QC criteria and procedures apply to the confirmation analysis as well.

9.0 GC Using Ion Trap Detector (GC/ITD) Confirmation Analysis

9.1 If specified in the project plans, a certain percentage of samples which have PCB congeners detected by dual column GC/ECD, shall be qualitatively and quantitatively confirmed by GC/ITD. GC/ITD analysis will be performed on an aliquot of the original extract. The relative percent difference (RPD) in the results of the two methods should be less than 50%.

10.0 Calculations

10.1 A quadratic weighted least squares regression model is used to calculate the concentration of the congeners in the sample extract. For values calculated below and above the calibration range, a straight line is projected using the slope calculated at the lowest and the highest point, respectively.

10.2 Calculate the concentration of congeners in water samples using the following equation for external standards. Response can be measured by automated peak height or peak area measurements from an integrator.

$$\textit{Concentration of each congener } C_x \textit{ (ng/L)} = \frac{(C_l)(V_t)}{(V_s)}$$

Where:

C_l = Concentration of congener in extract (ng/ml)

V_t = Volume of total extract (ml); take into account any dilutions

V_s = Volume of water extracted (L)

10.3 Calculate the concentration of congeners in the sediment samples using the following equation for external standards. Response can be measured automated peak height or peak area measurements from an integrator.

$$\textit{Concentration of each congener } C_x \textit{ (µg/kg)} = \frac{(C_l)(V_t)}{(W_s) \times 1000 \textit{ (ng/µg)}}$$

Where:

C_l = Concentration of congener in extract (ng/ml)

V_t = Volume of total extract (ml); take into account any dilutions

W_s = Weight (dry) of sample extracted (kg)

10.4 Calculate the concentration of congeners in the particulate samples using the following equation for external standards. Response can be measured by automated peak height or peak area measurements from an integrator.

$$\textit{Concentration of each congener } C_x \textit{ (ng/filter)} = \frac{(C_l)(V_t)}{\textit{filter}}$$

Where:

C_l = Concentration of congener in extract (ng/ml)

V_t = Volume of total extract (ml); take into account any dilutions

10.5 Match retention times of peaks in the standards with peaks in the sample. Calculate the concentration of every identifiable PCB congener peak unless interference with individual peaks persists after cleanup.

10.6 Calculation for Surrogate and Matrix Spike Recoveries

$$\textit{Percent Recovery} = \frac{Qd}{Qa} \times 100\%$$

Where:

Q_d = quantity determined by analysis (for matrix spike recoveries only, Q_d = Spike Sample Results - Sample Results)

Qa = quantity added to sample.

Be sure all dilutions are taken into account.

10.7 Report results in nanograms per liter (ng/l) for water samples, micrograms per kilogram (μg/kg) for sediment samples, and nanograms total (ng total) for particulate samples without correction for recovery data. Sediment samples are reported on a dry weight basis.

11.0 Reporting

11.1 In order to report the low concentration of some PCB congeners in the presence of higher concentrated congeners as expected in environmental samples, the range of acceptable reporting limits is extended at both the lower and higher calibration range. The following guidelines are used to give maximum information for each analysis.

11.1.1 PCB congeners will be reported down to 0.1 μg/L in extract, except for monobiphenyls at 0.5 μg/L in extract.

11.1.2 PCB congeners will be reported up to two times the concentration of the ICAL5 standard.

11.1.3 Matrix spike samples will not be diluted to put spiked compounds below two times the ICAL5 standard.

11.2 Quantitation Column Determination

11.2.1 The following decision tree is used to determine which column should be used for the quantitation of each PCB congener that is detected on both the primary and confirmation columns.

11.2.1.1 If the PCB congener elutes as a resolved peak on both columns and 5 initial calibration data points are available for quantitation on both columns, report the lower concentration results.

11.2.1.2 If the PCB congener elutes as a resolved peak on both columns and less than 5 initial calibration data points are available for quantitation on one or both of the columns, report the result from the column with the greater number of initial calibration data points. If the same number of initial calibration data points are available for each column, report the result from the primary column.

11.2.1.3 If the PCB congener is resolved on only one of the columns, report the result from the column where resolution is achieved and qualify with S.

11.2.1.4 If the PCB congener is not resolved on either column, calculate a result by subtracting out the concentration of the coeluting congeners, report this value, and quality with X.

11.3 Definition of Laboratory Qualifiers

11.3.1 U - Compound not detected above reporting limit of 0.1 ppb in extract for all PCB congeners (0.5 ppb in extract for the monochlorinated biphenyls). The reported value is the calibrated quantitation limit (CQL).

11.3.2 J - Compound detected above reporting limit, but below calibration range.

This qualifier is applied to any positive result that is less than the lowest calibration standard.

11.3.3 E - Compound concentration exceeds the calibration range.

This qualifier is applied to any positive result that exceeds the calibration range. The laboratory may report some congeners with concentrations up to twice the concentration in the highest calibration standard, in order to report some very low concentrations and low quantitation limits.

11.3.4 S - Specific column result used for quantitation due to confirmation column coelution.

This qualifier designates congeners whose results are always quantitated from a specific column due to coelution with congeners or surrogates on the other column. The S qualifier precludes the P qualifier since a %D between columns is excepted to be greater than 25% due to coelution on one column.

11.3.5 T - Tentative identification, specific column result used with no confirmation information.

This qualifier designates congeners which could not be confirmed due to an interferant (or surrogate) peak, however, there is good reason to believe its presence.

11.3.6 X - Estimated concentration due to coelution on both columns.

This qualifier designates congeners which coelute with congeners or surrogates on both analytical columns. In order to report a concentration for the congener of interest, the concentrations of the coeluting congeners are subtracted from it.

11.3.7 P - Confirmation column result exceeds reported result by more than 25%.

This qualifier is applied to a congener result if the concentration on the quantitation and confirmation columns exceed the percent difference (%D) criteria of 25.

11.3.8 H - Specific column or estimated result exceeds confirmation result by more than 25% despite expected confirmation coelution.

This qualifier is applied to a congener result if the result from the quantitation column exceeds the confirmation result by more than 25 %D, even though the confirmation column result was expected to be greater due to coelution on the confirmation column.

12.0 Quality Control

12.1 Method Blanks

12.1.1 A method blank is a volume of reagent water, baked sodium sulfate, or a filter (depending on matrix of associated samples), carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

12.1.2 Method blank analysis must be performed at the following frequency:

- each 20 samples in a Sample Delivery Group that are of similar matrix; or

- whenever 20 or fewer samples from the same Sample Delivery Group are extracted by the same procedure, at the same time, whichever is more frequent. The associated method blank is analyzed on each GC system used to analyze samples.

12.1.3 It is the Laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

12.1.4 For the purposes of this protocol, an acceptable laboratory method blank must contain no confirmed PCB congener detected above the CQL and must not have any interferences detected above 5 times the CQL on the primary or confirmation columns. Due to limited sample volumes, if a method blank fails the quality control limits the quality assurance officer must be notified immediately to discuss corrective action. Corrective action may include re-extraction and re-analysis of all associated samples. Reextractions should be performed within the 5 days of sample collection, whenever possible. The Laboratory Manager, or his designee, must address problems and solutions in a Case Narrative.

12.1.5 The Laboratory must report results of method blank analysis.

12.1.6 The Laboratory must report ALL sample concentration data as UNCORRECTED for blank contamination.

12.2 Surrogate Spike (SS) Analysis

12.2.1 Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before extraction in order to monitor preparation and analysis of samples.

12.2.2 The surrogate spiking compounds, tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN) are used to fortify each sample, matrix spike, matrix spike duplicate, matrix spike blank, and blank prior to extraction. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocols will not be permitted.

12.2.3 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls within the advisory recovery limits of 60 to 150 percent. If the recovery of the surrogate TCMX is less than 10 percent, the laboratory must re-extract and re-analyze the sample.

12.2.4 The Laboratory shall report surrogate recovery data for the following:

- Method Blank Analysis
- Sample Analysis
- Matrix Spike/Matrix Spike Duplicate Analyses
- Matrix Spike Blank

12.3 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

12.3.1 In order to evaluate the matrix effect of the sample upon the analytical methodology, the PCB congener matrix spiking solution is to be used for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes. The makeup of the spiking solution is specified in the appropriate matrix-specific extraction SOPs.

12.3.2 A matrix spike and matrix spike duplicate must be performed on a sample once:

- each 20 samples in a Sample Delivery Group of a similar matrix;

  or

- each 14 calendar day period during which samples in a Sample Delivery Group were received (said period beginning with the receipt of the first sample in that Sample Delivery Group); whichever is most frequent.

12.3.3 The analytical protocols in the SOPs for the extraction and cleanup of PCBs from environmental matrices stipulate the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples. Samples requiring optional

dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

12.3.4 Individual component recoveries of the matrix spike are calculated using the equation below. Advisory recovery limits for all PCB matrix spiking compounds are 60 to 150 percent.

$$\textit{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100\%$$

Where:

SSR = Spike Sample Results

SR = Sample Result

SA = Spiked Added from Spiking Mix

12.3.5 The Laboratory is required to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using the following equation. The advisory limit for MS/MSD relative percent difference is 40 percent.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

12.3.6 The results for the non-spiked PCB congeners in the MS and MSD shall be reported along with the matrix spike percent recoveries. This will assist data users in assessing analytical precision of non-spiked congeners.

12.4 Matrix Spike Blank (MSB)

12.4.1 A Matrix Spike Blank (MSB) is a volume of reagent water or granular sodium sulfate that has been spiked with the PCB congener matrix spiking solution (see the accompanying SOPs for extraction of PCBs from sediment and water for composition of PCB congener matrix spiking solution, Appendices A-1 through A-3) and subject to the entire extraction and analysis procedure. The MSB is used to assess the performance of the method.

12.4.2 A Matrix Spike Blank must be extracted and analyzed once:

- each 20 samples in Sample Delivery Group of a similar matrix;

  or

- each 14 calendar day period during which samples in a Sample Delivery Group were received (said period beginning with the receipt of the first sample in that Sample Delivery Group), whichever is most frequent.

12.4.3 The PCB congener matrix spiking solution should be added to the blank so that the resultant concentrations of PCB congeners in the Matrix Spike Blank are approximately 10 to 15 times the MDL determined for each congener.

12.4.4 The Matrix Spike Blank must be evaluated by determining whether the concentration (measured as percent recovery) falls within the advisory recovery limits of 60 to 150 percent. If 10 percent or more of the congeners fall outside of the advisory recovery limits, the laboratory must re-extract and re-analyze the matrix spike blank and all associated samples. The laboratory should re-prepare a new matrix spike solution if re-extraction and re-analysis does not generate MSB recoveries within the advisory limits.

12.4.5 The Laboratory shall report Matrix Spike Blank recovery data for all matrix spiking compounds.

12.5 PCB Calibration, Quantitation, and Confirmation QA/QC Requirements

Section 12.5 through 12.7 summarizes ongoing QC activities involved with PCB congener analysis that were detailed in Sections 12.1, 12.2, 12.3, and 12.4, and describes the additional QA/QC procedures required during the analysis of PCB congeners that are not covered in Sections 12.1, 12.2, 12.3, and 12.4.

12.5.1 The Laboratory must perform the following:

- Method Blank analysis as per Section 12.1.
- Surrogate spike of all standards, samples, blanks, matrix spikes, matrix spike duplicates, and matrix spike blanks as per Section 12.2.
- Matrix Spike/Matrix Spike duplicate analysis as per Section 12.3.
- Matrix Spike Blank as per Section 12.4.

12.6 Primary and Confirmation GC Column Analysis

12.6.1 Primary Analysis establishes whether or not PCB congeners are present in the sample, and establishes a tentative identification of each PCB congener. Quantitation may be performed on the Primary Analysis if the analysis meets all of the QC criteria specified for quantitation. NOTE: To determine that no PCB congeners are present at or above the method detection limit is a form of quantitation. Confirmation Analysis is to confirm the identification and quantitation of all PCB congeners tentatively identified in the Primary Analysis.

12.6.2 Prepare the Calibration Standards at the 5 concentration levels described in Section 4.4. Analyze the five Calibration Standards sequentially at the beginning of each analytical sequence (see Section 12.5.4.1).

12.6.3 Before performing any sample analysis, the laboratory is required to establish the retention time window for each PCB congener to be determined and the surrogate spike compounds. These retention time windows are used to make tentative identification of the PCBs during sample analysis. Establish retention time windows as follows:

- Analyze a five-level initial calibration curve on each column and calculate the retention time mean.

- The retention time windows are calculated from the mean initial calibration retention time at ±0.25 minutes for the mono- through the tetra-chlorinated congeners and TCMX and at ±0.35 minutes for all other PCB congeners and OCN.

12.6.4 Establish a calibration curve for each column using a quadratic least squares regression model.

12.6.5 Calculate the correlation coefficient for the calibration curve for each PCB congener and surrogate. The correlation coefficient must be ≥0.995 (see Section 5.1).

12.6.6 Calculate the percent relative standard concentration error (%RSCE) for each PCB congener and surrogate using all five calibration points. The %RSCEs must be less than 15% with the exception of monochlorobiphenyls and two other PCB congeners which must be less than 20% (see Section 5.1).

12.6.7 Resolution Criteria - The ICAL3 standard is used to measure the resolution of peaks. The following resolution criteria must be met:

- SB-Octyl-50 - Should have greater than 50% resolution for the following pairs of PCB congeners:

  1. BZ #5 and BZ #8
  2. BZ #41 and BZ #40
  3. BZ #183 and BZ #185
  4. BZ #209 and octachloronaphthalene

- HP-5 - Should meet the following resolution criteria for the following pair of PCB congeners:

  1. BZ #4 and BZ# 10, which coelute, and TCMX should have greater than 25% resolution.
  2. BZ #31 and BZ #28 should have greater than 25% resolution.
  3. BZ #84 and BZ#101 should have greater than 50% resolution.
  4. BZ #206 and octachloronaphthalene should have greater than 50% resolution.

Calculate the percent resolution as follows:

$$\textit{Percent Resolution} = \frac{H_s - H_v}{H_s} \times 100\%$$

Where:

H_v = the height of the valley between the peaks

H_s = the height of the smaller peak

12.7 Sample Analysis

12.7.1 Samples are analyzed per the sequence described below.

1. Instrument Blank
2. ICAL1
3. ICAL2
4. ICAL3
5. ICAL4
6. ICAL5 (0 hour for first analytical window)
7. Instrument Blank
8. Samples
9. Instrument Blank (first injection after 12 hours)
10. OCAL3 (0 hour for second analytical window)
11. Samples
12. Instrument Blank (first injection after 12 hours)
13. Repeat the above sequence starting with OCAL3 (step 10 above). Continue as long as quality control requirements are met and no significant adjustments are made to the analytical system.
14. PCB analysis sequence must end with the analyses of OCAL3.

12.7.2 The retention time shift for the surrogate standards must be evaluated after the analysis of each sample. The retention time shift may not exceed ± 0.25 minutes for TCMX or ± 0.35 minutes for OCN.

Calculate the retention time shift for each of the surrogate standards using the following equation:

$$\Delta RT = RT_I - RT_s$$

Where:

RT_I = mean retention time of the surrogate standard in the initial calibration

RT_s = absolute retention time of the surrogate standard in the sample

12.7.3 If one or more compounds have a response greater than full scale, the extract requires dilution according to the specifications in Section 7.9.3.

12.7.4 If the samples are analyzed on two or more instruments, all appropriate standards and method blanks pertaining to those samples must be analyzed on each instrument.

12.7.5 Method blanks (extracted with each set of samples) must be analyzed on every GC on which the samples are analyzed.

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12.14 Fischer, R. and K. Ballschmiter, Congener-specific Identification of Technical PCB Mixtures by Capillary Gas Chromatography on a n-octyl-methyl Silicone Phase (SB-Octyl-50) with Electron Capture-and Mass-Selective Detection; Fresenios Z Anal. Chem. (1989) 335:457-463.

12.15 NYSDEC ASP, December 1991. Method 91-11, Analytical Method for Total PCBs and PCB congeners by Fused Silica Capillary Column Gas Chromatography with Electron Capture Detector (GC/ECD).

12.16 USEPA Contract Laboratory Program, Statement of Work for Organics Analysis, Document Number OLM01.8, 8/91.

Table 1
PCB Congeners for Calibration Standards

BZ#	Structure
1	2-Chlorobiphenyl
2	3-Chlorobiphenyl
3	4-Chlorobiphenyl
4	2,2'-Dichlorobiphenyl
5	2,3-Dichlorobiphenyl
6	2,3'-Dichlorobiphenyl
7	2,4'-Dichlorobiphenyl
8	2,4'-Dichlorobiphenyl
9	2,5-Dichlorobiphenyl
10	2,6-Dichlorobiphenyl
12	3,4-Dichlorobiphenyl
15	4,4'-Dichlorobiphenyl
16	2,2',3-Trichlorobiphenyl
18	2,2',5-Trichlorobiphenyl
19	2,2',6-Trichlorobiphenyl
22	2,3,4'-Trichlorobiphenyl
25	2,3',4-Trichlorobiphenyl
26	2,3',5-Trichlorobiphenyl
27	2,3',6-Trichlorobiphenyl
28	2,4,4'-Trichlorobiphenyl
29	2,4,5-Trichlorobiphenyl
31	2,4',5-Trichlorobiphenyl
37	3,4,4'-Trichlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl
41	2,2',3,4-Tetrachlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
53	2,2',5,6'-Tetrachlorobiphenyl

Table 1 - cont'd

BZ#	Structure
56	2,3,3',4'-Tetrachlorobiphenyl
66	2,3',4,4'-Tetrachlorobiphenyl
70	2,3',4',5-Tetrachlorobiphenyl
75	2,4,4',6-Tetrachlorobiphenyl
77	3,3',4,4'-Tetrachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl
83	2,2',3,3',5-Pentachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl
85	2,2',3,4,4'-Pentachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl
92	2,2',3,5,5'-Pentachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl
97	2,2',3',4,5-Pentachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl
105	2,3,3',4,4'-Pentachlorobiphenyl
107	2,3,3',4',5-Pentachlorobiphenyl
115	2,3,4,4',6-Pentachlorobiphenyl
118	2,3',4,4',5-Pentachlorobiphenyl
119	2,3',4,4',6-Pentachlorobiphenyl
122	2',3,3',4,5-Pentachlorobiphenyl
123	2',3,4,4',5-Pentachlorobiphenyl
126	3,3',4,4',5-Pentachlorobiphenyl
128	2,2',3,3',4,4'-Hexachlorobiphenyl
129	2,2',3,3',4,5-Hexachlorobiphenyl
136	2,2',3,3',6,6'-Hexachlorobiphenyl
137	2,2',3,4,4',5-Hexachlorobiphenyl
138	2,2',3,4,4',5'-Hexachlorobiphenyl
141	2,2',3,4,5,5'-Hexachlorobiphenyl
149	2,2',3,4',5',6-Hexachlorobiphenyl
151	2,2',3,5,5',6-Hexachlorobiphenyl
153	2,2',4,4',5,5'-Hexachlorobiphenyl
157	2,3,3',4,4',5'-Hexachlorobiphenyl

Table 1 - cont'd

BZ#	Structure
158	2,3,3',4,4',6-Hexachlorobiphenyl
167	2,3',4,4',5,5'-Hexachlorobiphenyl
170	2,2',3,3',4,4',5-Heptachlorobiphenyl
171	2,2',3,3',4,4',6-Heptachlorobiphenyl
177	2,2',3,3',4',5,6-Heptachlorobiphenyl
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
185	2,2',3,4,5,5',6-Heptachlorobiphenyl
187	2,2',3,4',5,5',6-Heptachlorobiphenyl
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
190	2,3,3',4,4',5,6-Heptachlorobiphenyl
191	2,3,3',4,4',5',6-Heptachlorobiphenyl
193	2,3,3',4',5,5',6-Heptachlorobiphenyl
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
196	2,2',3,3',4,4',5',6-Octachlorobiphenyl
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
199	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
201	2,2',3,3',4',5,5',6-Octachlorobiphenyl
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
208	2,2',3,3',4,,5,5',6,6'-Nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl

Note: BZ# = Ballschmiter and Zell System

Table 2A
GC Operating Conditions - Option A

Hewlett Packard 5890 Series II with packed column injection port and dual electron capture detectors

Configuration

A five meter x 0.32 mm ID deactivated guard column is installed into the packed column injection port using a Restek Uniliner. The guard column is connected via a SGE VSIS-2 inlet splitter to the two analytical columns (SB-OCTYL-50 and HP-5) which are connected to an electron capture.

The HP7673 auto-sampler is set-up for slow injection with a dwell time of 4 sec.

Oven Conditions

Initial Temperature	-	100°C
Initial Time	-	0.50 min
Ramp Rate	-	10°/min
Temperature 2	-	160/170°C
Time 2	-	0 min
Ramp Rate 2	-	2.5°C/min
Temperature 3	-	197°C
Time 3	-	0 min
Ramp Rate 3	-	1.5°/min
Temperature 4	-	270°C
Time 4	-	4.0 min

Note: Temperature 2 will vary in order to achieve chromatographic resolution between tetrachloro-m-xylene and BZ#9 on the SB-octyl-50 column and BZ#4 & 10 and tetrachloro-m-xylene on the HP-5 column.

Other Conditions

Injection Port Temperature	-	250°C
Detector Temperatures	-	310°C
Injection Amount	-	3 ul
Carrier Gas	-	hydrogen, constant back pressure at 38 psi
ECD Make-up	-	100 ml/min 5% Argon/methane

Table 2B
GC Operating Conditions - Option B

Hewlett Packard 5890 Series II, with programmable on-column injection port and dual electron capture detectors.

Configuration

A five meter x 0.53mm ID deactivated guard column is installed into the on-column injector. The guard column is connected to a glass Universal "Y" connector to the two analytical columns (SB-Octyl-50 and RTX-5) which are each connected to an electron capture detector.

Oven Conditions

Initial Temperature	-	100°C
Initial Time	-	0.5 min
Ramp Rate 1	-	20°/min
Temperature 2	-	150°C
Time 2	-	0 min
Ramp Rate 2	-	2.5°C/min
Temperature 3	-	197°C
Time 3	-	0 min
Ramp Rate 3	-	1.5°/min
Temperature 4	-	275°C
Time 4	-	0 min

Injection Port Program

Injection Port Temperature Program

Initial Temperature	-	63°C
Initial Time	-	0.5 min
Ramp Rate	-	20°C/min
Final Temperature	-	250°C
Final Time	-	5 min

Other Conditions

Detector Temperatures	-	310°C
Injection Amount	-	3.0 ul
Carrier Gas	-	hydrogen, constant back pressure at 38 psi
ECD Make-up	-	100 ml/min 5% Argon/methane

Table 3
Numbering System For PCB Congeners

BZ#	Structure
-	Biphenyl
1	2-Chlorobiphenyl
2	3-Chlorobiphenyl
3	4-Chlorobiphenyl
4	2,2'-Dichlorobiphenyl
5	2,3-Dichlorobiphenyl
6	2,3'-Dichlorobiphenyl
7	2,4-Dichlorobiphenyl
8	2,4'-Dichlorobiphenyl
9	2,5-Dichlorobiphenyl
10	2,6-Dichlorobiphenyl
11	3,3'-Dichlorobiphenyl
12	3,4-Dichlorobiphenyl
13	3,4'-Dichlorobiphenyl
14	3,5-Dichlorobiphenyl
15	4,4'-Dichlorobiphenyl
16	2,2',3-Trichlorobiphenyl
17	2,2',4-Trichlorobiphenyl
18	2,2',5-Trichlorobiphenyl
19	2,2',6-Trichlorobiphenyl
20	2,3,3'-Trichlorobiphenyl
21	2,3,4-Trichlorobiphenyl
22	2,3,4'-Trichlorobiphenyl
23	2,3,5-Trichlorobiphenyl
24	2,3,6-Trichlorobiphenyl
25	2,3',4-Trichlorobiphenyl
26	2,3',5-Trichlorobiphenyl
27	2,3',6-Trichlorobiphenyl
28	2,4,4'-Trichlorobiphenyl
29	2,4,5-Trichlorobiphenyl
30	2,4,6-Trichlorobiphenyl
31	2,4',5-Trichlorobiphenyl

Table 3 - cont'd

BZ#	Structure
32	2,4',6-Trichlorobiphenyl
33	2',3,4-Trichlorobiphenyl
34	2',3,5-Trichlorobiphenyl
35	3,3',4-Trichlorobiphenyl
36	3,3',5-Trichlorobiphenyl
37	3,4,4'-Trichlorobiphenyl
38	3,4,5-Trichlorobiphenyl
39	3,4',5-Trichlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl
41	2,2',3,4-Tetrachlorobiphenyl
42	2,2',3,4'-Tetrachlorobiphenyl
43	2,2',3,5-Tetrachlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl
45	2,2',3,6-Tetrachlorobiphenyl
46	2,2',3,6'-Tetrachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyl
48	2,2',4,5-Tetrachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl
50	2,2',4,6-Tetrachlorobiphenyl
51	2,2',4,6'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
53	2,2',5,6'-Tetrachlorobiphenyl
54	2,2',6,6'-Tetrachlorobiphenyl
55	2,3,3',4-Tetrachlorobiphenyl
56	2,3,3',4'-Tetrachlorobiphenyl
57	2,3,3',5-Tetrachlorobiphenyl
58	2,3,3',5'-Tetrachlorobiphenyl
59	2,3,3',6-Tetrachlorobiphenyl
60	2,3,4,4'-Tetrachlorobiphenyl
61	2,3,4,5-Tetrachlorobiphenyl
62	2,3,4,6-Tetrachlorobiphenyl
63	2,3,4',5-Tetrachlorobiphenyl
64	2,3,4',6-Tetrachlorobiphenyl

Table 3 - cont'd

BZ#	Structure
65	2,3,5,6-Tetrachlorobiphenyl
66	2,3',4,4'-Tetrachlorobiphenyl
67	2,3',4,5-Tetrachlorobiphenyl
68	2,3',4,5'-Tetrachlorobiphenyl
69	2,3',4,6-Tetrachlorobiphenyl
70	2,3',4',5-Tetrachlorobiphenyl
71	2,3',4',6-Tetrachlorobiphenyl
72	2,3',5,5'-Tetrachlorobiphenyl
73	2,3',5',6-Tetrachlorobiphenyl
74	2,4,4',5-Tetrachlorobiphenyl
75	2,4,4',6-Tetrachlorobiphenyl
76	2',3,4,5-Tetrachlorobiphenyl
77	3,3',4,4'-Tetrachlorobiphenyl
78	3,3',4,5-Tetrachlorobiphenyl
79	3,3',4,5-Tetrachlorobiphenyl
80	3,3',5,5'-Tetrachlorobiphenyl
81	3,4,4',5-Tetrachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl
83	2,2',3,3',5-Pentachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl
85	2,2',3,4,4'-Pentachlorobiphenyl
86	2,2',3,4,5-Pentachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl
88	2,2',3,4,6-Pentachlorobiphenyl
89	2,2',3,4,6-Pentachlorobiphenyl
90	2,2',3,4',5-Pentachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl
92	2,2',3,5,5'-Pentachlorobiphenyl
93	2,2',3,5,6-Pentachlorobiphenyl
94	2,2',3,5,6'-Pentachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl
96	2,2',3,6,6'-Pentachlorobiphenyl
97	2,2',3',4,5-Pentachlorobiphenyl

Table 3 - cont'd

BZ#	Structure
98	2,2',3',4,6-Pentachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl
100	2,2',4,4',6-Pentachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl
102	2,2',4,5,6'-Pentachlorobiphenyl
103	2,2',4,5',6-Pentachlorobiphenyl
104	2,2',4,6,6'-Pentachlorobiphenyl
105	2,3,3',4,4'-Pentachlorobiphenyl
106	2,3,3',4,5-Pentachlorobiphenyl
107	2,3,3',4',5-Pentachlorobiphenyl
108	2,3,3',4,5'-Pentachlorobiphenyl
109	2,3,3',4,6-Pentachlorobiphenyl
110	2,3,3',4',6-Pentachlorobiphenyl
111	2,3,3',5,5'-Pentachlorobiphenyl
112	2,3,3',5,6-Pentachlorobiphenyl
113	2,3,3',5',6-Pentachlorobiphenyl
114	2,3,4,4',5-Pentachlorobiphenyl
115	2,3,4,4',6-Pentachlorobiphenyl
116	2,3,4,5,6-Pentachlorobiphenyl
117	2,3,4',5,6-Pentachlorobiphenyl
118	2,3',4,4',5-Pentachlorobiphenyl
119	2,3',4,4',6-Pentachlorobiphenyl
120	2,3',4,5,5'-Pentachlorobiphenyl
121	2,3',4,5',6-Pentachlorobiphenyl
122	2',3,3',4,5-Pentachlorobiphenyl
123	2',3,4,4',5-Pentachlorobiphenyl
124	2',3,4,5,5'-Pentachlorobiphenyl
125	2',3,4,5,6'-Pentachlorobiphenyl
126	3,3',4,4',5-Pentachlorobiphenyl
127	3,3',4,5,5'-Pentachlorobiphenyl
128	2,2',3,3',4,4'-Hexachlorobiphenyl
129	2,2',3,3',4,5-Hexachlorobiphenyl
130	2,2',3,3',4,5'-Hexachlorobiphenyl

Table 3 - cont'd

BZ#	Structure
131	2,2',3,3',4,6-Hexachlorobiphenyl
132	2,2',3,3',4,6'-Hexachlorobiphenyl
133	2,2',3,3',5,5'-Hexachlorobiphenyl
134	2,2',3,3',5,6-Hexachlorobiphenyl
135	2,2',3,3',5,6'-Hexachlorobiphenyl
136	2,2',3,3',6,6'-Hexachlorobiphenyl
137	2,2',3,4,4',5-Hexachlorobiphenyl
138	2,2',3,4,4',5'-Hexachlorobiphenyl
139	2,2',3,4,4',6-Hexachlorobiphenyl
140	2,2',3,4,4',6'-Hexachlorobiphenyl
141	2,2',3,4,5,5'-Hexachlorobiphenyl
142	2,2',3,4,5,6-Hexachlorobiphenyl
143	2,2',3,4,5,6'-Hexachlorobiphenyl
144	2,2',3,4,5',6-Hexachlorobiphenyl
145	2,2',3,4,6,6'-Hexachlorobiphenyl
146	2,2',3,4',5,5'-Hexachlorobiphenyl
147	2,2',3,4',5,6-Hexachlorobiphenyl
148	2,2',3,4',5,6'-Hexachlorobiphenyl
149	2,2',3,4',5',6-Hexachlorobiphenyl
150	2,2',3,4',6,6'-Hexachlorobiphenyl
151	2,2',3,5,5',6-Hexachlorobiphenyl
152	2,2',3,5,6,6'-Hexachlorobiphenyl
153	2,2',4,4',5,5'-Hexachlorobiphenyl
154	2,2',4,4',5,6'-Hexachlorobiphenyl
155	2,2',4,4',6,6'-Hexachlorobiphenyl
156	2,3,3',4,4',5-Hexachlorobiphenyl
157	2,3,3',4,4',5'-Hexachlorobiphenyl
158	2,3,3',4,4',6-Hexachlorobiphenyl
159	2,3,3',4,5,5'-Hexachlorobiphenyl
160	2,3,3',4,5,6-Hexachlorobiphenyl
161	2,3,3',4,5',6-Hexachlorobiphenyl
162	2,3,3',4',5,5'-Hexachlorobiphenyl
163	2,3,3',4',5,6-Hexachlorobiphenyl

Table 3 - cont'd

BZ#	Structure
164	2,3,3',4',5',6-Hexachlorobiphenyl
165	2,3,3',5,5',6-Hexachlorobiphenyl
166	2,3,4,4',5,6-Hexachlorobiphenyl
167	2,3',4,4',5,5'-Hexachlorobiphenyl
168	2,3',4,4',5',6-Hexachlorobiphenyl
169	3,3',4,4',5,5'-Hexachlorobiphenyl
170	2,2',3,3',4,4',5-Heptachlorobiphenyl
171	2,2',3,3',4,4',6-Heptachlorobiphenyl
172	2,2',3,3',4,5,5'-Heptachlorobiphenyl
173	2,2',3,3',4,5,6-Heptachlorobiphenyl
174	2,2',3,3',4,5,6'-Heptachlorobiphenyl
175	2,2',3,3',4,5',6-Heptachlorobiphenyl
176	2,2',3,3',4,6,6'-Heptachlorobiphenyl
177	2,2',3,3',4',5,6-Heptachlorobiphenyl
178	2,2',3,3',5,5',6-Heptachlorobiphenyl
179	2,2',3,3',5,6,6'-Heptachlorobiphenyl
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
181	2,2',3,4,4',5,6-Heptachlorobiphenyl
182	2,2',3,4,4',5,6'-Heptachlorobiphenyl
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl
185	2,2',3,4,5,5',6-Heptachlorobiphenyl
186	2,2',3,4,5,6,6'-Heptachlorobiphenyl
187	2,2',3,4',5,5',6-Heptachlorobiphenyl
188	2,2',3,4',5,6,6'-Heptachlorobiphenyl
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
190	2,3,3',4,4',5,6-Heptachlorobiphenyl
191	2,3,3',4,4',5',6-Heptachlorobiphenyl
192	2,3,3',4,5,5',6-Heptachlorobiphenyl
193	2,3,3',4',5,5',6-Heptachlorobiphenyl
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
196	2,2',3,3',4,4',5',6-Octachlorobiphenyl

Table 3 - cont'd

BZ#	Structure
197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
199	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
201	2,2',3,3',4',5,5',6-Octachlorobiphenyl
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
203	2,2',3,4,4',5,5',6-Octachlorobiphenyl
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl

Appendix A-5
Congener Specific Determination of Polychlorinated Biphenyls (PCBs) in Hexane Extracts by Capillary Column Gas Chromatography/Ion Detector (GC/ITD) - Confirmation Analyses

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Appendix A-5

CONGENER SPECIFIC DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) IN HEXANE EXTRACTS BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/ION TRAP DETECTOR (GC/ITD) - CONFIRMATION ANALYSES

1.0 Scope and Application

1.1 This method, which is a modified version of EPA Method 680, describes procedures for confirmation of polychlorinated biphenyls (PCBs) in hexane extracts by fused silica capillary column gas chromatography with ion trap full scan mass spectrometric detection. This method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. The preparation procedures for all the extracts are described in the appropriate matrix-specific SOPs. The extracts should be analyzed by GC/ECD prior to GC/ITD analysis to determine the appropriate concentration or dilution. Sample extracts for analysis will be selected after review of ECD data in order to maximize data utility and minimize nondetects.

1.2 Detection limits vary among method analytes and with sample matrix, sample preparation, procedures, condition of the GC/ITD system, type of data acquisition, and individual samples. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 5-10 times higher than that of a monochlorobiphenyl. A monochlorobiphenyl can be identified and accurately measured when the injected extract aliquot contains 10 pg and full-range data are acquired. The detection limit for total PCBs will depend on the number of individual PCB congeners present.

2.0 Summary of Method

2.1 Sample extract components are separated with fused silica capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization, ion trap detector (ITD). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential.

2.2 Nine selected PCB congeners are used as calibration standards, and two internal standards, chrysene-d_{12} and phenanthrene-d_{10}, are used to calibrate ITD response to PCBs.

3.0 Interferences

3.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment. All of these materials must be demonstrated to be free of interferences under the analytical conditions by routine analysis of laboratory method blanks.

3.2 For PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences. Capillary column GC retention times and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs.

4.0 Apparatus and Materials

4.1 Computerized GC/ITD System

4.1.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns.

4.1.2 Mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required ITD scan rate must allow acquisition of at least or five data points for each monitored ion while a sample component elutes from the GC. The ITD must produce a mass spectrum meeting all criteria for $\leq$20 ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.

4.1.3 An interfaced data system (DS) is required to acquire, store, reduce, and output mass spectral data. The DS must be capable of searching a data file for specific ions and plotting ion abundances versus time or spectrum number to produce selected ion current profiles (SICPs). Also required is the capability to obtain chromatographic peak areas between specific times or spectrum numbers in SICPs. Total data acquisition time per cycle should be $\geq$0.5 s and must not exceed 1.5 s.

4.2 GC COLUMN - A 30 m x 0.25 mm ID fused silica capillary column coated with a 0.5 μm or thicker film crosslinked phenyl methyl silicone (such as Durabond-5 (DB-5), J and W Scientific, Rancho Cordova, CA) or polydiphenyl vinyl dimethyl siloxane (such as SE-54, Alltech Associates, Deerfield, IL) is required. Operating conditions known to produce acceptable results with these columns are shown in Table 1. Retention times have been reported (6) for all 209 PCB congeners with an SE-54 column, which provides the same retention order for PCBs and essentially the same separation capabilities as a DB-5 column.

4.3 Balance - Analytical capable of weighing accuracy $\pm$ 0.01 mg.

5.0 Reagents

5.1 Solvents

5.1.1 High purity, distilled-in-glass hexane. For precise injections with splitless injectors and capillary columns, all samples and standards should be contained in the same solvent. Effects of minor variations in solvent composition (i.e., small percentage of another solvent remaining in hexane extracts) are minimized with the use of internal standards. (External standard calibration is not acceptable.)

5.1.2 Nanograde ethyl ether shown to be free of peroxides.

5.2 ITD Performance Check Solution -- Prepare a 1 ng/ul solution of decafluorotriphenylphosphine (DFTPP) in an appropriate solution.

5.3 Internal Standards - Chrysene-d_{12} and phenanthrene-d_{10} are used as internal standards. They are added to each sample extract just before analysis and are contained in all concentration calibration and performance check solutions.

5.4 PCB Concentration Calibration Compounds - The nine individual PCB congeners listed in Table 2 are used as concentration calibration compounds for PCB determinations. One isomer at each level of chlorination is used as the concentration calibration standard for all other isomers at that level of chlorination, except that decachlorobiphenyl (Cl_{10}) is used for both Cl_9 and Cl_{10} isomer groups.

5.5 Target Compound Mixture - In order to evaluate instrument performance, a standard mixture containing all of the target compounds and surrogates will be analyzed at the beginning and end

of each analytical sequence. This will be used to evaluate quantitation and to provide retention time data for the target compounds. Each target compound will be at a concentration of 0.1 ng/μl with the exception of the monochlorobiphenyls (0.5 ng/μl) and the surrogates (0.2 ng/μl). This solution will be based on CAL5 used for ECD initial calibration.

5.6 PCB Solutions

5.6.1 Stock Solutions of PCB Calibration Congeners - Prepare a stock solution of each of the nine PCB concentration calibration congeners and each of the three retention time congeners at a concentration of 1 μg/μl in hexane. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C if solutions are not to be used right away. Solutions are stable indefinitely is solvent evaporation is prevented.

CAUTION: Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration. Solutions should be stored with the smallest possible volume of headspace, and opening vials should be minimized.

5.6.2 PCB Primary Dilution Standard - Take aliquots of the stock solutions of the nine PCB concentration calibration congeners and mix together in the proportions of one part of each solution of the Cl_1 (#1), Cl_2 (#5), and Cl_3 (#29) congeners, two parts of each solution of the Cl_4 (#50), Cl_5 (#87), and Cl_6 (#154) congeners, three parts of each solution of the Cl_7 (#188) and Cl_8 (#200) congeners, and five parts of the Cl_{10} (#209) congener solution. This will provide a primary dilution standard solution of the composition shown in Table 3. Calculate the concentration in μg/μl; use three significant figures. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C. Mark the meniscus on the vial wall to monitor solution volume during storage; solutions are stable indefinitely if solvent evaporation is prevented.

5.7 Internal Standard (IS) Solution

5.7.1 Weigh 0.75 mg $\pm$ 0.001 mg each of phenanthrene-d_{10} and chrysene-d_{12}; dissolve in hexane and dilute to 10 ml in a volumetric flask. (Concentration of each IS = 75 ng/μl.)

5.8 CALS for Data Acquisition -- One set of five solutions for determination of PCB congeners is needed. Appropriate concentrations of CALs are given in Table 4. The solutions are prepared by diluting appropriate primary dilution standards and adding appropriate volume of IS solution.

5.9 Calculate the concentration (two significant figures) of each component in each solution. Note: Concentrations presented in the attached tables are only approximate.

5.10 Laboratory Performance Check Solution -- The Medium CAL is used as the laboratory performance check solution (LPC) to verify response factors and to demonstrate GC resolution and ITD performance.

6.0 Calibration

Initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. No samples are to be analyzed until acceptable initial calibration is demonstrated and documented. After initial calibration is successfully performed, continuing calibration check standards are required at the beginning and end of each 12-hour period during which analyses are performed.

6.1 Initial Calibration

6.1.1 Calibrate and tune the ITD with standards and procedures prescribed by the manufacturer with any necessary modifications to meet USEPA requirements.

6.1.2 Inject a 1-μl or 2-μl aliquot of the 1 ng/μl DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 5), the ITD must be hardware tuned to meet all criteria before proceeding with calibration.

6.1.3 Calibration - Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s.

6.1.4 Performance Criteria

6.1.4.1 PCB Data

6.1.4.1.1 GC separation -- Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.

6.1.4.1.2 ITD sensitivity -- Signal/noise ratio of $\geq$5 for m/z 499 of PCB congener #209, Cl_{10}-PCB, and for m/z 241 of chrysene-d_{12}.

6.1.4.1.3 ITD calibration -- Abundance of ≥70% and ≤95% of m/z 500 relative to m/z 498 for congener #209, Cl_{10}-PCB.

6.1.5 Replicate Analyses of CALS - If all performance criteria are met, analyze each of the other four concentration calibration solutions.

6.1.6 Response Factor Calculation

6.1.6.1 Calculate response factors (RFs) for each PCB calibration congener and surrogate compound relative to both ISs, phenanthrene-d_{10} and chrysene-d_{12}:

$$RF = A_x Q_{is} / A_{is} Q_x$$

where A_x = integrated ion abundance of quantitation ion for a PCB calibration congener or a surrogate compound,

A_{is} = integrated ion abundance of m/z 240, the quantitation ion when chrysene-d_{12} is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-d_{10} is used as the internal standard,

Q_{is} = injected quantity of chrysene-d_{12} or phenanthrene-d_{10},

Q_x = injected quantity of PCB calibration congener or surrogate compound. RF is a unitless number, units used to express quantities must be equivalent.

6.1.7 Response Factor Reproducibility - For each PCB calibration congener and surrogate compound, calculate the mean RF from analyses of each of the five CALs. When the RSD exceeds 20%, analyze additional aliquots of appropriate CALs to obtain an

acceptable RSD of RFs over the entire concentration range, or take action to improve GC/ITD performance.

6.1.8 Record a spectrum of each CAL component.

6.2 Continuing Calibration Check

6.2.1 With the following procedures, verify initial calibration at the beginning and end of each 12-hour period during which analyses are to be performed.

6.2.2 A GC/ITD analytical sequence is as follows:

DFTPP	-	ITD toning compound
CAL3	-	Midlevel GC/ITD standard used as beginning calibration check.
ICAL5	-	High level GC/ECD standard containing all target analytes used to establish retention times.
CAL400	-	Aroclor standard containing 100 ng/ml of each of the following aroclor mixtures: AR1221, AR1242, AR1254, and AR1260. Used to verify scan windows and retention times.
Samples	-	Up to eight samples may be analyzed.
CAL3	-	Ending calibration check.
ICAL5	-	Ending retention time check.
CAL400	-	Ending aroclor standard.

6.2.3 Calibrate and tune the ITD with standards and procedures prescribed by the manufacturer.

6.2.4 Analyze a 1-μl or 2-μl aliquot of the DFTPP solution and ensure acceptable ITD calibration and performance (Table 5).

6.2.5 Inject a 1-μl or 2-μl aliquot of the Medium CAL and analyze with the same conditions used during Initial Calibration.

6.2.6 Demonstrate acceptable performance for criteria described in Sect. 6.1.4.

6.2.7 Determine that neither the area measured for m/z 240 for chrysene-d_{12} nor that for m/z 188 for phenanthrene-d_{10} has decreased by more than 30% from the area measured in the

most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration.

6.2.8 Response Factor Reproducibility - For an acceptable Continuing Calibration Check, the measured RF for each analyte/surrogate compound must be within ±20% of the mean value calculated (section 6.1.6) during Initial Calibration. If not, remedial action must be taken; recalibration may be necessary.

6.2.9 Analyte Retention Time Reproducibility - Demonstrate and document acceptable (section 6.1.8) reproducibility and absolute retention times of appropriate PCB congeners.

6.2.10 Remedial actions must be taken if criteria are not met; possible remedies are:

6.2.10.1 Check and adjust GC and/or ITD operating conditions.

6.2.10.2 Clean or replace injector liner.

6.2.10.3 Flush column with solvent according to manufacturers instructions.

6.2.10.4 Break off a short portion (approximately 0.33 m) of the column; check column performance by analysis of performance check solution.

6.2.10.5 Replace GC column; performance of all initial calibration procedures then required.

6.2.10.6 Adjust ITD for greater or lesser resolution.

6.2.10.7 Calibrate ITD mass scale.

6.2.10.8 Prepare and analyze new concentration calibration/performance check solution.

6.2.10.9 Prepare new concentration calibration curve(s).

7.0 Quality Control

7.1 Method Blank - The method blanks associated with the samples are not required to be analyzed by this method, since the GC/ITD analyses are performed on 10% of the samples as a confirmation of the GC/ECD analyses.

7.2 Calibration -- Included among initial and containing calibration procedures are numerous quality control checks to ensure that valid data are acquired (see section 6). Continuing calibration checks are accomplished with results from analysis, the medium level calibration solution.

7.2.1 If some criteria are not met for a Continuing Calibration Check after a 12-h period during which samples were analyzed, those samples must be reanalyzed. Those criteria are: GC performance (section 6.1.4), ITD calibration as indicated by the closing calibration check and ITD sensitivity as indicated by area of internal standards.

7.2.2 When other criteria in section 6.2 are not met, results for affected analytes must be labeled as suspect to alert the data user of the observed problem. Included among those criteria are: response factor check for each analyte or PCB calibration congener and retention time reproducibility.

7.3 Laboratory Surrogate Spike

7.3.1 Measure the concentrations of the tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN) in every sample and blank if there is sufficient sensitivity.

8.0 Procedures

8.1 GC/ITD Analysis

8.1.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to the appropriate volume, depending on anticipated analyte concentrations. Add an appropriate volume of the internal standard stock solution. Internal standard concentration for data acquisition = 0.75 ng/μl of extract.

8.1.2 Inject a 1-μl or 2-μl aliquot of the extract into the GC operated under the same conditions used to produce acceptable results during calibration.

8.1.3 Acquire mass spectral data using the same data acquisition time and ITD operating conditions previously used to determine response factors.

8.1.4 Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately.

8.1.5 For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

8.2 Identification Procedures

8.2.1 Using the ions shown in Table 7 for PCBs examine selected ion current profiles (SICPs) to locate internal standards and PCBs for each isomer group. Use the RRT window data in Table 6 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)

8.2.2 Data - Obtain appropriate SICPs for IS quantitation and confirmation ions and for the quantitation and confirmation ions for each PCB isomer group.

8.2.3 PCB Analytes

8.2.3.1 For all PCB candidates, confirm the presence of an $(M-70)^+$ ion cluster by examining SICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.

8.2.3.2 For Cl_3-CL_7 isomer groups, examine SICPs or spectra for intense $(M+70)^+$ ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data shown that this is not a potential problem for other PCB isomer groups.) If this interference occurs, a correction can be made. Obtain and record the area of the appropriate ion (Table 7) for the candidate PCB isomer group. Use the

information in Table 8 to correct the measured abundance of M^+. For example, if a Cl_7-PCB and a Cl_5-PCB candidate coelute, the Cl_7-PCB will contribute to the ion measured for m/z 326 and m/z 324, the quantitation and confirmation ions, respectively, for a Cl_5-PCB. Obtain and record the area for m/z 322 (the lowest mass ion in the $M+-70)^+$ ion cluster of a Cl_5-PCB fragment produced by a Cl_7-PCB). To determine the m/z 326 and m/z 324 areas produced by the Cl_5 PCB, calculate the Cl_7-PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for m/z 322 should be subtracted from the area measured for m/z 324, and 108% of the m/z 322 area should be subtracted from the area measured for m/z 326 (Table 8).

8.2.3.3 For Cl_2-Cl_8-PCB candidates, examine SICPs or spectra for intense $(M+35)^+$ ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because or the natural abundance of ^{13}C. (This interference will be small and can be neglected except when measuring the area of a small amount of PCB coeluting with a large amount of another PCB containing one more chlorine.) To correct for this interference, obtain and record the area for the appropriate ion (Table 9) from the $(M-1)^+$ ion cluster, and subtract 13.5% of the area measured for the $(M-1)^+$ ion from the measured area of the quantitation ion. For example, for Cl_5-PCB candidates, obtain and record the area of m/z 325; subtract 13.5% of that area from the measured area of m/z 326.

8.2.4 All Analytes - Use SICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 7). If acceptable ratios are not obtained, a coeluting or partially coeluting compound may be interfering. Examination of data from several scans may provide information that will allow application of additional background corrections to improve the ion ratio.

8.3 Identification Criteria

8.3.1 Internal Standards

8.3.1.1 Chrysene -d_{12} - the abundance of m/z 241 relative to m/z 240 must be $\geq 15\%$ and $\leq 25\%$, and these ions must maximize simultaneously. The

area measured for m/z 240 must be within 30% of the area measured during the most recent calibration.

8.3.1.2 Phenanthrene-d_{10} - the abundance of m/z 189 relative to m/z 188 must be $\geq$10% and $\leq$22%, and these ions must maximize simultaneously. The area measured for m/z 188 must be within 30% of the area measured during the most recent acceptable calibration.

8.3.1.3 Retention time must be within $\pm$10 s of that observed during the most recent acceptable calibration.

8.3.2 Data for PCBs

8.3.2.1 Absolute retention times of surrogate compounds must be within $\pm$10 s of that measured during the last previous continuing calibration check.

8.3.2.2 Quantitation and confirmation ions for each PCB isomer group must maximize within $\pm$1 scan of each other.

8.3.2.3 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

8.3.2.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation area must be within limits shown in Table 7; at least one ion in the $(M-70)^+$ ion cluster must be present.

9.0 Calculations

9.1 From appropriate SICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.

9.2 For PCBs, sum the areas for all isomers identified at each level of chlorination (e.g., sum all quantitation ions areas for Cl_4-PCBs). Also determine the area of each individual target PCB congener.

9.3 Calculate the concentrations of each surrogate compound, PCB isomer group and individual PCB congener using the formula:

$$C_x = (A_x \cdot Q_{is}) / (A_{is} \cdot RF \cdot W)$$

where C_x = concentration (μg/kg or μg/L) of surrogate compound, a PCB isomer group, or an individual PCB congener.

A_x = the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination, or the quantitation ion area for one PCB congener.

A_{is} = the area of the internal standard quantitation ion, m/z 240 for chrysene-d_{12} or m/z 188 for phenanthrene-d_{10}.

Q_{is} = quantity (μg) of internal standard added to the extract before GC/ITD analysis.

RF = calculated response factor for the surrogate compound or the PCB calibration compound for the isomer group (level of chlorination).

W = dry weight (kg) of sample extracted. If a liquid sample was extracted, W becomes V, the volume (L) of water extracted, and concentration units become micrograms per liter.

9.3.1 Use the mean RF calculated during Initial Calibration. CAUTION: For PCB analyses with automated data interpretation a linear fit algorithm will produce erroneous concentration data.

9.3.2 For PCBs, use the RF relative to chrysene-d_{12} for penta through deca isomers and the RF relative to phenanthrene-d_{10} for mono through tetra isomers.

9.4 Report calculated values to two significant figures.

9.5 When standards of known composition are analyzed, calculate the percent method bias using the equation:

$$B = 100 (C_s - C_r) / C_t$$

where C_s = measured concentration (in micrograms per kilogram or micrograms per liter),

C_t = theoretical concentration (i.e., the quantity added to the sample aliquot/weight or volume of sample aliquot).

Note: The bias value retains a positive or negative sign.

10.0 Automated Identification and Measurement

10.1 Special software can be used for automated identification and measurement of PCBs (7) and pesticides. Unprocessed GC/ITD data are handled without human interaction with the software operating on the dedicated computer. However, the laboratory must demonstrate that the current data reduction and reporting software has been verified for accuracy according to U.S. EPA Good Automated Laboratory Practices (GALP). Software must be revalidated whenever changes are made to the software.

11.0 References

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Table 1
Recommended GC Operating Conditions

Capillary column:	30 m x 0.25 mm ID, 0.5 micron film thickness, fused silica DB-5 (or equivalent) splitless mode
Initial temperature:	90°C, initial hold - 2 minutes
Temperature program 1:	10°C/minute for 6 minutes
Temperature program 2:	3°C/minute to 290 C
Final temperature:	290°C, final hold - 4 minutes
Injection port temperature:	210°C
Detector temperature:	300°C

Table 2
PCB Congeners Used as Calibration

PCB Isomer Group	Congener Number[a]	
Concentration Calibration Standard		
Monochlorobiphenyl	1	2
Dichlorobiphenyl	5	2,
Trichlorobiphenyl	29	2,4
Tetrachlorobiphenyl	50	2,
Pentachlorobiphenyl	87	2,2
Hexachlorobiphenyl	154	2,2',
Heptachlorobiphenyl	188	2,2'
Octachlorobiphenyl	200	2,2',
Nonachlorobiphenyl[b]	–	
Decachlorobiphenyl	209	2,2',

[a] Numbered according to the system of Ballschmiter and Zell (2).
[b] Decachlorobiphenyl is used as the calibration congener for both isomer groups.

Table 3
PCB Primary Dilution Solution

PCB Cong.	Isomer Group	Stock Sol. Conc. mg/ml	Proportion for Primary Dil. Sol.	Primary Dil. Std. Conc. ng/ul
#1	Cl_1	1.0	1 part	50
#5	Cl_2	1.0	1 part	50
#29	Cl_3	1.0	1 part	50
#50	Cl_4	1.0	2 parts	100
#87	Cl_5	1.0	2 parts	100
#154	Cl_6	1.0	2 parts	100
#188	Cl_7	1.0	3 parts	150
#200	Cl_8	1.0	3 parts	150
#209	Cl_{10}	1.0	5 parts	250
			Total 20 parts	

Table 4
Composition and Approximate Concentrations of
Calibration Solutions for Data Acquisition for PCB Determinations

	Concentration (ng/ul)				
Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
Cal. Congeners					
Cl_1 (#1)	0.01	0.05	0.1	0.2	0.5
Cl_2 (#5)	0.01	0.05	0.1	0.2	0.5
Cl_3 (#29)	0.01	0.05	0.1	0.2	0.5
Cl_4 (#50)	0.02	0.10	0.2	0.4	1.0
Cl_5 (#87)	0.02	0.10	0.2	0.4	1.0
Cl_6 (#154)	0.02	0.10	0.2	0.4	1.0
Cl_7 (#188)	0.03	0.15	0.3	0.6	1.5
Cl_8 (#200)	0.03	0.15	0.3	0.6	1.5
Cl_{10} (#209)	0.05	0.25	0.5	1.0	2.5
Internal Standards					
Chrysene-d_{12}	0.75	0.75	0.75	0.75	0.75
Phenanthrene-d_{10}	0.75	0.75	0.75	0.75	0.75

Table 5
Ion Abundance Criteria for Bis(perfluorophenyl)phenyl Phosphine (Decafluorotriphenylphosphine, DFTPP)

Mass (m/z)	Relative Abundance Criteria	Purpose of Checkpoint[1]
51	10-80% of the base peak	low mass sensitivity
68	<2% of mass 69	low mass resolution
70	<2% of mass 69	low mass resolution
127	10-80% of the base peak	low-mid mass sensitivity
197	<2% of mass 198	mid-mass resolution
198	base peak or >50% of 442	mid-mass resolution and sensitivity
199	5-9% of mass 198	mid-mass resolution and isotope ratio
275	10-60% of the base peak	mid-high mass sensitivity
365	>1% of the base peak	baseline threshold
441	present and < mass 443	high mass resolution
442	base peak or >50% of 198	high mass resolution and sensitivity
443	15-24% of mass 442	high mass resolution and isotope ratio

[1] All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

From EPA Method 525.

Table 6

Retention Time Data for PCB Isomer Groups and Calibration Congeners

Isomer Group	RRT Window[a]	Cal. Cong. Number	Cal. Cong. RRT[a]
Monochlorobiphenyls	0.30-0.35	1	0.30
Dichlorobiphenyls	0.38-0.50	5	0.43
Trichlorobiphenyls	0.46-0.64	29	0.54
Tetrachlorobiphenyls	0.55-0.82	50	0.56
Pentachlorobiphenyls	0.64-0.92	87	0.80
Hexachlorobiphenyls	0.75-1.1	154	0.82
Heptachlorobiphenyls	0.88-1.2	188	0.88
Octachlorobiphenyls	0.99-1.21	200	1.03
Nonachlorobiphenyls	1.16-1.28	--	--
Decachlorobiphenyl	1.3	209	1.3

[a] Retention time relative to chrysene-d_{12} with a 30 m X 0.31 mm ID SE-54 fused silica capillary column and the following GC conditions: splitless injection at 80°C; hold for 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°C/min to 310°C.

Table 7

Quantitation, Confirmation, and Interference Check Ions for PCBs and Internal Standards

Analyte/ Internal Std.	Nom. MW	Quant. Ion	Confirm. Ion	Expected Ratio[a]	Accept. Ratio[a]	M-70 Confirm. Ion	Interference Check Ions M+70	Interference Check Ions M+35
PCB Isomer Group								
Cl_1	188	188	190	3.0	2.5-3.5	152[b]	256	222
Cl_2	222	222	224	1.5	1.3-1.7	152	292	256
Cl_3	256	256	258	1.0	0.8-1.2	186	326	290
Cl_4	290	292	290	1.3	1.1-1.5	220	360	326
Cl_5	324	326	324	1.6	1.4-1.8	254	394	360
Cl_6	358	360	362	1.2	1.0-1.4	288	430	394
Cl_7	392	394	396	1.0	0.8-1.2	322	464	430
Cl_8	426	430	428	1.1	0.9-1.3	356	498	464
Cl_9	460	464	466	1.3	1.1-1.5	390	--	498
Cl_{10}	494	498	500	1.1	0.9-1.3	424	--	--
Internal Standards								
Chrysene-d_{12}	240	240	241	5.1	4.3-5.9	--	--	--
Phenanthrene-d_{10}	188	188	189	6.6	6.0-7.2	--	--	--

[a] Ratio of quantitation ion to confirmation ion.

[b] Monodichlorobiphenyls lose HCl to produce anion at m/z 152.

Table 8

Correction for Interference of PCB Containing Two Additional Chlorines

Candidate Isomer Group	Quant. Ion	Confirm. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant. Ion Area	% of Meas. Ion Area to be Subtracted from Confirm. Ion Area
Trichlorobiphenyls	256	258	254	99%	33%
Tetrachlorobiphenyls	292	290	288	65%	131%
Pentachlorobiphenyls	326	324	322	108%	164%
Hexachlorobiphenyls	360	362	356	161%	71%
Heptachlorobiphenyls	394	396	390	225%	123%

Table 9
Correction for Interference of PCB Containing One Additional Chlorine

Candidate Isomer Group	Quant. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant. Ion Area
Dichlorobiphenyls	222	221	13.5%
Trichlorobiphenyls	256	255	13.5%
Tetrachlorobiphenyls	292	289	17.4%
Pentachlorobiphenyls	326	323	22.0%
Hexachlorobiphenyls	360	357	26.5%
Heptachlorobiphenyls	394	391	30.9%
Octachlorobiphenyls	430	425	40.0%

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Appendix A-6
Standard Operating Procedure Data Validation for Congener Specific Determination of Polychlorinated Biphenyls (PCBs) by Gas Chromatography/Electron Capture Detector (GC/ECD)

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Appendix A-6

STANDARD OPERATING PROCEDURE DATA VALIDATION FOR CONGENER SPECIFIC DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD)

METHOD SUMMARY

The analytical methods described in the Appendices of the Sampling and Analysis Plan/Quality Assurance Project Plan (SAP/QAPjP) for the Hudson River PCB Reassessment RI/FS are extraction, cleanup, and analytical methods for PCB congeners. Briefly, polychlorinated biphenyl (PCB) congeners are extracted from water, sediment, particulate (filter), or biota samples, the resulting hexane extracts are processed through various cleanup procedures, and then are analyzed by fused silica capillary column gas chromatography with electron capture detector (GC/ECD). The PCBs are identified and quantitated by congener. A subset of the sample extracts (approximately 5% to 10% of the samples, as specified in the SAP/QAPjP) will be analyzed to confirm the congener identification by gas chromatography/ion trap detector (GC/ITD). The GC/ITD analyses will also provide quantitative confirmation of the congeners. This standard operating procedure (SOP) details the process of validation for samples analyzed for congener specific determination of PCBs by GC/ECD. The data validation SOP for the GC/ITD analyses is provided in Appendix A-7.

I. DATA COMPLETENESS

The data deliverables for these methods will include, at a minimum:

- Case narrative
- Chain-of-Custody records
- Sample and method blank results summaries (Form I or equivalent)
- Surrogate recovery summaries for each matrix (Form II or equivalent)
- Matrix spike/matrix spike duplicate recovery summaries for each matrix (Form III or equivalent)
- Method blank summary (Form IV or equivalent)
- Retention time window summaries (Form 6D or equivalent)
- Initial and continuing calibration summaries (Forms 6E and 7E or equivalents)
- Analytical sequence summary (Form VIII or equivalent)
- Silica gel check standard (Form 9A or equivalent)

- Sample log-in and SDG file (CSF) inventory sheets (DC-1 and DC-2 or equivalent)
- Raw data for each field sample, blank, and quality control (QC) sample, including chromatograms, quantitation reports, and sample preparation logbook summaries

The specific sample weight, final volume, and cleanup procedures used for each sample should be clearly identified in the data package.

II. HOLDING TIMES

A. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of sample preparation or analysis, as appropriate.

B. Criteria

Both samples and extracts must be preserved at 4° C. Water, sediment, and particulate samples must be extracted within 7 days of sample collection and the extract must be analyzed within 40 days following extraction according to EPA's "Laboratory Data Validation Functional Guidelines for Evaluating Organic Analyses" (February 1, 1988) and Region II's, "SOP No. HW-6, Revision 8" (January, 1992).

C. Evaluation Procedure

Holding times are calculated by comparing the sampling date on the EPA SAS Packing List/Chain-of-Custody records with dates of extraction and analysis listed on the Form I (or equivalent).

D. Action

If the holding times are exceeded, flag all positive and nondetect results as estimated (G and UG, respectively) and document in the validation report that holding times were exceeded. If the extraction or analytical holding times are grossly exceeded (i.e., by more than 14 days), either upon initial analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data. The reviewer may determine that the nondetect data are unusable (R).

III. INSTRUMENT PERFORMANCE

A. Objective

Instrument performance criteria are established to verify that adequate chromatographic resolution and retention time stability are achieved throughout the analytical sequence, both of which are crucial for qualitative identification of the congeners. These are method criteria and therefore these criteria must be met in all circumstances.

B. Criteria

1. Resolution Check

The midpoint initial calibration standard and all continuing calibration standards are used to measure the resolution of peaks.

On the SB-octyl-50 column, the following pairs of congeners and/or surrogates must have chromatographic resolution greater than 50%:

BZ#5 and BZ#8
BZ#41 and BZ#40
BZ#183 and BZ#185
BZ#209 and OCN

On the HP-5 column, the following groups of congeners and/or surrogates must meet the specified chromatographic resolution:

BZ#4 + BZ#10 and TCMX	25%
BZ#31 and BZ#28	25%
BZ#84 and BZ#101	50%
BZ#206 and OCN	50%

$$\% \ Resolution = \frac{H_p - H_v}{H_p} \times 100\%$$

where,

H_v = the height of the valley between the peaks

H_p = the maximum height of the smaller peak

2. Retention Time Windows

The laboratory must report retention time window data for each congener for each GC column used to analyze the sample (see Form 6D or equivalent). The retention time windows are calculated from the average initial calibration retention times (RTs) at ± 0.25 minutes for the mono- through tetra-chlorinated congeners and ± 0.35 minutes for all other congeners.

3. Surrogate Retention Time Check

The retention times (RTs) of the surrogates tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN) in each analysis must be compared to the retention time windows established from the initial calibration. The retention time windows are calculated from the average initial calibration RTs as ± 0.25 minutes for TCMX and

±0.35 minutes for OCN. TCMX and OCN RTs must be within the established retention time windows for all samples and standards.

C. **Evaluation Procedure**

1. Check the raw data to verify that the resolution criteria stated above have been met.

2. Check the raw data and Form 6D to verify that the congener retention time windows are correctly calculated and reported, and that all PCB congener RTs in standards are within the established retention time windows.

3. Check the raw data and Form VIII to verify that the surrogate retention times are within the established retention time windows.

D. **Action**

1. If the resolution criteria are not met, a close examination of the chromatography is necessary to confirm adequate separation of the congeners. If adequate separation of any congener pair is not achieved, the reviewer may use professional judgment to estimate (G) the positive congener results for a poorly resolved pair, if there is sufficient evidence that the congeners are present in the sample.

2. Retention time windows are used in qualitative identification. If the standards do not fall within the retention time windows, the associated sample results should be carefully evaluated. All samples analyzed after the last in-control standard are potentially affected.

   a. If the affected sample chromatograms contain peaks which may be of concern (close to or within the retention time window), the reviewer may use the following information to confirm or refute the presence of the deviant congeners:

      - pattern recognition, based on other samples in the sample delivery group (SDG);
      - the surrogate retention times to create "revised" windows based on relative retention times;
      - the congener retention times of other standards to create "revised" windows, based on possible retention time shifts; and
      - matrix spike results which confirm the magnitude of the retention time shift.

   If the results (positive or nondetect) cannot be confirmed, the data should be qualified as unusable (R).

   b. The data validation narrative should identify any calculations or professional judgments used by the reviewer and the resultant impact on data usability. In addition, the data validation report should contain the calculations and comparisons generated by the reviewer necessary to support qualification of the data for data usability assessments.

3. If the retention times for TCMX or OCN are not within the established retention time windows, the results may be flagged as unusable (R) for that sample, but qualification of the associated data in that analytical sequence is left up to the professional judgment of the reviewer. The chromatograms from both columns should be carefully reviewed to determine if any coeluting interferences are present.

IV. CALIBRATION

A. Objective

Compliance requirements for satisfactory instrument calibration are established to verify that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance prior to the analysis of samples, and the continuing calibration checks document satisfactory maintenance and adjustment of the instrument over a specific time period.

B. Criteria

1. Initial Calibration

An initial calibration at five concentration levels (excluding blanks) must be performed. A quadratic weighted (1/x, x = concentration) least squares regression model is generated from the data. The correlation coefficient for the curve must be ≥ 0.995. The percent relative standard concentration error (%RSCE) of the five calibration points must not exceed 20% for mono chlorinated congeners and 15% for all other congeners. These criteria apply to both analytical columns.

2. Analytical Sequence

At the beginning of each analytical sequence, a five-concentration level calibration must be performed ending with an instrument blank. An instrument blank and a mid-level calibration standard, in that order, must be analyzed after every 12 hours of analysis as a continuing calibration check.

3. Continuing Calibration

The calculated vs. nominal concentration for each congener must be within 25 percent difference (%D) for all PCB congeners and surrogates.

C. Evaluation Procedure

1. Inspect the initial calibration summary forms (see, Form 6E or equivalent) and verify agreement with the raw GC data. Recalculate 10%[1] of the data to verify the reported %RSCEs. If errors are detected, a more comprehensive recalculation must be performed. Verify that correlation coefficients are ≥ 0.995.

[1]The recalculations of the data (usually 10%) should be performed during the initial review of a congener package to validate the reporting software. If errors are detected, a more thorough review of the data is required. Once the reporting software has been validated random spot checks of the data should be performed in lieu of the 10% criterion.

$$\% \text{ concentration error} = \frac{C_{calc} - C_{nom}}{C_{nom}}$$

% RSCE = SD(n-1) of the % concentration errors for five calibration points

SD = standard deviation
C_{calc} = calculated concentration of each analyte in the standards
C_{nom} = nominal (true) concentration of each analyte

2. Verify that the appropriate analytical sequence (see, Form VIII or equivalent) was followed.

3. Inspect the continuing calibration summary forms (see, Form 7E or equivalent) and verify agreement with the raw data. Using the following formula, recalculate approximately 10% of the reported %Ds for verification.

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100\%$$

where,

C_{nom} = nominal (true) concentration of each analyte

C_{calc} = calculated concentration of each analyte from the analyses of the standard

D. **Action**

1. If a correlation coefficient is less than 0.995, qualify all associated positive and nondetect results as estimated (G and UG, respectively). If an initial calibration %RSCE is greater than 15% (20% for mono-chlorinated congeners), qualify associated positive quantitative results as estimated (G) for that congener. If the %RSCE exceeds 50%, the reviewer should use professional judgment to determine the extent and direction of bias, and estimate (UG) the nondetect results if deemed necessary. If, in the judgment of the reviewer, the variability in instrument response is so great that all positive and nondetect results are suspect, the data may be qualified as unusable (R).

2. If the standards or instrument blanks have not been analyzed at the required frequency, the reviewer must use professional judgment to determine the severity of the effect and qualify the data accordingly.

3. If the %D between the true concentration and the calculated concentration of a congener is greater than 25%, flag associated positive quantitative results as estimated (G) for that

congener. If the %D exceeds 50%, the reviewer should use professional judgment to determine the extent and direction of the bias, and estimate (UG) the nondetect results if deemed necessary. If, in the judgment of the reviewer, the variability in instrument response is so great that all positive and nondetect results are suspect, the data may be qualified as unusable (R).

The reviewer must carefully document the qualification of data, with detailed descriptions of potential biases.

V. BLANKS

A. Objective

The reason for assessment of blank analysis results is to evaluate the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any field and laboratory blanks associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

B. Criteria

Any confirmed or unconfirmed congeners present in any blank at concentrations greater than the reporting level will be reviewed in conjunction with sample data to determine possible level of blank contamination in the samples.

C. Evaluation Procedure

Review the results of all associated blanks (method, field, and instrument blanks), including all raw data. Verify that the blanks contain less than the reporting level for all confirmed and unconfirmed congeners. The laboratory may not report a blank contaminant that does not meet the requirements for congener confirmation. Since, the presence of unknown peaks in a blank within the retention time windows of congeners may result in false positives or results which may be biased high, these will also be evaluated.

Verify that a method blank was extracted for each matrix for each SDG. Verify that instrument blanks have been analyzed prior to each continuing calibration standard.

D. Action

Action in the case of unsuitable blank results depends on the circumstances and the origin of the blank. No positive results should be accepted unqualified unless the concentration of the compound in the sample exceeds 5 times (5x) the amount found in the associated blank. In instances where more than one blank is associated with a given sample, qualification should be based on comparison with the associated blank having the highest concentration of the contaminant. The results must not be corrected by subtracting the blank value. Specific actions are as follows:

1. If a congener is found in the blank but not found in the sample(s), no action is taken.

2. Any congener detected in a sample and also detected in any associated blank, must be qualified when the sample concentration is less than 5x the associated blank concentration. The positive results are qualified as also detected in the associated blank (B).

   The reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be accounted for when applying the 5x criteria, such that a comparison of the total amount of each contaminant is made.

   In addition, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. For example, contamination can be introduced into the instrument by hexane dilution of the extract. Such occurrences can be determined when contaminants are not present in the initial analyses but are present in dilutions. If the reviewer determined that the source of the contamination is not from the sample itself, then the data should be qualified. In these cases, the 5x rule does not apply and the sample value should be qualified as possibly biased high due to contamination (B).

3. Non-congener contamination can also occur, such as phthalate contamination introduced by pierced vial septa between initial and re-analyses. Contamination may result in false positives or higher calculated concentrations on one column due to coelution of the contaminant with a native congener. False negatives are also possible, as a contaminant may obscure the detection of a congener within the retention time windows. Professional judgment may be used to evaluate the severity of the contamination effects and need for qualification of associated sample results.

   The reviewer must carefully document all actions taken due to contamination.

VI. SURROGATE RECOVERY

A. Objective

Acceptable laboratory performance in analyzing individual samples may be evaluated by the review of recoveries of surrogate spikes. Surrogate compounds are spiked into all samples prior to sample extraction. The evaluation of surrogate spike recoveries is not necessarily straightforward. Surrogate recoveries for each sample may be hampered due to matrix effects. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present unique problems, the review and validation of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines.

B. Criteria

The advisory limits for TCMX and OCN recoveries are 60-150%.

C. **Evaluation Procedure**

Check the raw data to verify the reported recoveries on the surrogate recovery form (see, Form II or equivalent). If recoveries are not within limits, check the raw data for possible interferences which may have affected surrogate recoveries.

D. **Action**

If the recovery of TCMX is outside of the control limits, the associated sample results and quantitation limits should be estimated (G and UG, respectively). However, professional judgment may be used to apply the qualifiers. Low recovery of TCMX but not OCN may indicate a problem with the concentration procedures, and therefore the possibility of a negative bias is more likely for the more volatile congeners, such as mono- and di-chlorobiphenyls. The nondetect results may be considered unusable (R) if the quantification limits are suspect. Low recoveries of both TCMX and OCN may indicate matrix effects if the blanks are unaffected, or a general method bias within the laboratory if all samples and blanks are affected.

If high recoveries are obtained, professional judgment should be used to determine appropriate action. A high bias may be caused by coeluting interferences or by a laboratory method bias.

If recoveries of zero (0%) are reported, the reviewer should examine the sample chromatogram to determine if the surrogates may be present, but slightly outside of the retention time windows. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the reviewer should investigate the qualitative validity of the analysis due to possible retention time shifts.

If the recovery of TCMX is less than 10%, qualify positive results as estimated (G) and nondetect results as unusable (R). The sample must be reextracted and reanalyzed. If the reextraction analysis has an acceptable surrogate recovery, report this sample; however, if the surrogate recovery is still less than 10%, report the original analysis.

VII. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A. **Objective**

Matrix spike (MS) and matrix spike duplicate (MSD) data are generated to determine long-term precision (relative percent difference and relative standard deviation) and accuracy (percent recoveries) of the analytical method on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples.

B. **Criteria**

1. The advisory limits for spiked congener recoveries are 60 - 150%. The advisory limit for relative percent difference (RPD) of spiked congeners in the MS/MSD pair is 40%.

2. For the sample and MS/MSD pair, the nonspiked congener precision criteria is 40% Relative Standard Deviation (RSD).

C. **Evaluation Procedure**

1. Verify the reported recoveries by reviewing Form III and the raw data and verify the calculations.

2. Compare all the nonspiked PCB congener results, which are ≥ calibrated quantitation limit (CQL), from the sample and MS/MSD pair and calculate %RSD.

$$\%RSD = \frac{SD}{\bar{x}} \times 100\%$$

where,

SD = standard deviation of the concentrations

$\bar{x}$ = mean concentration

D. **Action**

No action is taken on the matrix spike/matrix spike duplicate recovery (MS/MSD) data alone to qualify an entire SDG. However, using informed professional judgment, the reviewer may use the MS/MSD recovery information in conjunction with other QC criteria to determine the need for some qualification of the data.

In those instances where it can be determined that the recovery results of the MS/MSD affect only the sample spiked, then qualification should be limited to this sample alone. However, it may be determined through the MS/MSD recovery results that a lab is having a systematic problem in the analysis of one or more congeners, which affects all associated samples.

Any nonspiked congeners that have a RSD > 40% should be estimated (G) in the sample result. If a congener is reported in the MS and/or MSD samples but is not detected in the nonspike sample, the nondetect sample result should be estimated (UG).

VIII. MATRIX SPIKE BLANK

A. **Objective**

The matrix spike blank (MSB) sample is reagent water spiked with matrix spike standard solution and matrix effects are assumed to be minimal. These QC data are generated to determine the stability of the matrix spike stock solution as well as long-term precision and accuracy of the analytical method. These data alone cannot be used to evaluate the precision and accuracy of individual samples.

B. **Criteria**

The advisory limits for congener recoveries are 60 - 150%. The associated samples and the matrix spike blank must be reextracted and reanalyzed if 10% or more of the spiked congeners fall outside of the 60-150% recovery limits. The laboratory should re-prepare a new matrix spike solution if re-extraction and re-analysis does not generate MSB recoveries within the advisory limits.

C. **Evaluation Procedure**

Verify the reported recoveries by reviewing the raw data and verify the calculations.

D. **Action**

No action is taken on the matrix spike blank data alone to qualify an entire SDG. However, using professional judgment, the reviewer may use the information in conjunction with other QC criteria to determine the need for qualification of the data.

Poor recovery may indicate an extraction deficiency or other bias in the laboratory procedures. The reviewer must determine the severity and effect of poor recoveries. The congeners in associated samples may be qualified as estimated (G) or unusable (R). All matrix spike blank samples should be evaluated to determine if there is systematic bias in the laboratory procedures during the analytical program.

IX. FIELD DUPLICATES

A. **Objective**

Field duplicate samples will be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates (or MS/MSD) which only measure laboratory performance for a specific matrix. It may also be expected that sediment field duplicates will have a greater variance than water field duplicates due to the difficulties associated with collecting representative river sediment field samples.

B. **Criteria**

The QAPjP requires that field duplicate results have less than 50% RPD.

C. **Evaluation Procedure**

Samples which are field duplicates are identified on the Sample Trip Reports. The reviewer should compare the PCB congener results which are ≥ calibrated quantitation limit (CQL) for each sample and calculate the RPD.

$$RPD = \frac{C_{ITD} - C_{ECD}}{(C_{ITD} + C_{ECD}) / 2} \times 100$$

where,

C_{ITD} = concentration of GC/ITD result.

C_{ECD} = concentration of GC/ECD result.

D. **Action**

Any congeners that have a RPD > 50% should be estimated (G). If a congener is reported in one field sample above the CQL but is not detected in the duplicate, estimate the positive result (G) in the original sample and the nondetect result (UG) in the field duplicate.

Significant differences in the concentrations or type of congeners reported in a field duplicate pair may indicate poor sample handling, possible mislabelling of sample containers, or high variability in the sample matrix.

X. COMPOUND IDENTIFICATION

A. **Objective**

Qualitative criteria for compound identification have been established to minimize the number of erroneous identifications of congeners. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

B. **Criteria**

Retention times of reported congeners must fall within the calculated retention time windows for the two chromatographic columns.

Selected samples will be analyzed by GC/ITD by the method detailed in Appendix A-5 (modified EPA Method 680) to verify congener identification.

C. **Evaluation Procedure**

Review the reported results and the associated raw data (chromatograms and data system printouts). Confirm the reported positive detects, using appropriate retention times and retention time windows, and verify that the congeners listed as "not detected" (nondetect) are correct.

Verify that positive identifications were confirmed on both GC columns. Verify that GC/ITD confirmation was performed on the specified samples.

For samples analyzed by GC/ITD, verify that the congeners identified by GC/ECD were confirmed by GC/ITD.

D. **Action**

If the qualitative criteria for two column confirmation are not met, all reported positive detects should be considered nondetects. The reviewer should use professional judgment to assign an appropriate quantitation limit. If the misidentified peak poses an interference with potential detection of a target congener, then the reported value should be considered nondetect and qualified as an estimated quantitation limit (UG).

As PCBs are multi-component mixtures, the reviewer may use professional judgment and knowledge of Aroclor congener composition to aid in congener identification and to qualify data based on the results of the GC/ITD analysis.

XI. COMPOUND QUANTITATION AND REPORTED DETECTION LIMITS

A. **Objective**

The objective is to verify that the reported quantitation results and reporting limits are accurate, as well as, to verify that the correct result and laboratory qualifiers are reported.

B. **Criteria**

1. Compound quantitation, as well as the adjustment of the reporting limits, must be calculated according to Appendix A-4.

2. Compound results and laboratory qualifiers must be reported according to Appendix A-4.

3. The results of the GC/ITD confirmation analyses as compared to the results of the GC/ECD analyses should be within 50% RPD for each congener that is at sufficient concentration to be detected by GC/ITD.

4. Any sample analyzed as a soil should contain $\leq$ 90% moisture.

C. **Evaluation Procedure**

1. Raw data should be examined to verify the correct calculation of sample results reported by the laboratory. Quantitation reports, chromatograms, and sample preparation log sheets should be compared to the reported positive results, laboratory qualifers, and quantitation limits.

2. Verify that the reporting limits have been adjusted to reflect all sample dilutions, concentrations, splits, cleanup activities, and dry weight factors that are not accounted for in the method. Verify that the reporting limits are consistent with the method detection limit (MDL) studies performed by the laboratory.

3. Verify that the GC/ITD congener results are within 50% RPD of those from the GC/ECD analyses.

4. Logbooks and Form Is should be examined to verify that the %moisture for each sample analyzed as a soil was ≤ 90%.

D. **Action**

If incorrect results, laboratory qualifiers, or quantitation limits have been reported by the laboratory, the reviewer should contact the laboratory and request resubmittals of all affected data.

Quantitation limits affected by large peaks should be flagged as unusable (R). The reviewer may also elect to provide an estimated detection limit for the affected congeners.

If the RPD between the GC/ECD and GC/ITD analyses exceeds 50% for a given congener, the positive result should be estimated (G). If the congener was detected in the sample extract by GC/ECD at sufficient concentration to be analyzed by GC/ITD, but is not found during the GC/ITD analysis, the positive GC/ECD results should be qualified as not confirmed by GC/ITD (Q). If the congener was detected in the sample extract by GC/ITD analysis, but was not detected by GC/ECD or was detected at a significantly lower concentration (< 1/5 of the GC/ITD value), then the positive or nondetect GC/ECD result should be qualified as (M). The reviewer should also examine the GC/ECD chromatogram to determine if the congener may have been misidentified due to two or more congeners within a retention time window or if the peak was obscured by a large positive interference. Discuss any finding in the validation narrative.

If the % moisture for a sample analyzed as a soil exceeds 90%, qualify all results for that sample as unusable (R).

XII. PERFORMANCE EVALUATION SAMPLE

A. **Objective**

The performance evaluation samples are analyzed to determine accuracy of the analytical method as performed by the laboratory. These data will not be used to qualify the results of individual samples but will be assessed as an indicator of overall laboratory performance of the method in the usability assessment.

B. **Criteria**

The advisory limits for PCB congener concentrations will be provided with the performance evaluation sample by the vendor.

C. **Evaluation Procedure**

Verify the reported results and calculations by reviewing the raw data.

D. Action

No action is taken during validation based on the performance evalution data. However, during the data usability assessment, the reviewer will use this information in conjunction with other QC criteria to determine the need for qualification of the data.

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Validation Worksheets
for PCB Congeners by GC/ECD

Laboratory:_____ Site: Hudson River PCB site

Case no.:_____ SDG no.:_____

Sampling date(s):_____ Number of samples:_____

Matrix:_____ Shipping date:_____

Date received by laboratory:_____

Sample IDs:_____

The general criteria used to determine the quality of the data were based on the examination of:

- Data completeness
- Holding times
- Instrument performance
- Calibration
- Blanks
- Surrogate recovery
- Matrix spike/matrix spike duplicate recoveries and precision
- Matrix spike blank recovery
- Field duplicate precision
- Compound identification
- Compound quantitation and reported detection limits
- Performance evaluation sample

Data validation was performed following the guidelines in "Data Validation Guidelines for Congener Specific Determination of Polychlorinated Biphenyls (PCBs)," Appendix A-6, SAP/QAPjP for the Hudson River PCB Reassessment RI/FS, January, 1993.

Overall Comments:_____

_____

_____

Definitions and qualifiers:

U - Not detected; the reported value is the calibrated quantitation limit (CQL).
J - Compound detected below calibration range
B - Compound was also detected in associated blank(s).
G - Estimated data due to quality control criteria
R - Reject data due to major exceedance of quality control criteria
M - Positive GC/ITD result was not detected by GC/ECD analysis or greater than 5 times GC/ECD result
Q - GC/ECD result at concentration within GC/ITD calibration range, but not confirmed by GC/ITD analysis

Primary Reviewer:_____ Date:_____

Senior Reviewer:_____ Date:_____

Data Completeness

Missing Information	Date Lab Contacted	Date Received

Holding Times

List all samples that exceeded the extraction holding time of 7 days from sample collection or the analysis holding time of 40 days following extraction.

Sample ID	Date Sampled	Date Extracted/ # of Days	Date Analyzed/ # of Days

Action: Qualify the positive and nondetect results as estimated (G, UG), if holding time exceeded. Professional judgment may be used to consider results unusable (R) if holding times are grossly exceeded (i.e., by more than 14 days).

Instrument Performance (Section 1)

Resolution

The midpoint initial and continuing calibration standards are used to evaluate the resolution of peaks. On the SB-octyl-50 column, the following congener pairs should have chromatographic resolution greater than 50%: BZ#5 and BZ#8, BZ#41 and BZ#40, BZ#183 and BZ#185, and BZ#209 and OCN. On the HP-5 column, the following pairs of congeners should meet the specified chromatographic resolution: BZ#4 + 10 and TCMX (25%), BZ#31 and BZ#28 (25%), BZ#84 and BZ#101 (50%), and BZ#206 and OCN (50%). List any PCB congener pairs that did not meet the resolution criteria stated above.

Standard ID	Date/Time of Analysis	PCB Congener Pair	% Resolution	Affected Samples

Action: If the resolution criteria are not met, a close examination of the chromatography is necessary. Qualification of the data is left up to the professional judgment of the reviewer. Discuss any actions below:

Instrument Performance (Section 2)

Standard Congener Retention Times

The retention time windows are calculated from the average initial calibration retention times (RTs) at ±0.25 minutes for mono- through tetra-chlorinated congeners and ±0.35 minutes for all other congeners.

List any PCB congeners in the standard analyses which have RTs outside the established retention time windows (RTWs).

Standard ID	Day/Time of Analysis	PCB Congener	RT	RTW	Affected Samples

Instrument Performance (Section 3)

Surrogate Retention Times

The surrogate retention time windows are calculated from the average initial calibration RTs as ±0.25 minutes for TCMX and ±0.35 minutes for OCN. List any surrogate in the sample or standard analyses which have RTs outside the established RTWs.

Sample/Standard ID	Date/Time of Analysis	Surrogate	RT	RTW

Action: If the RTs for TCMX or OCN are not within established RTWs, the analysis may be qualified as unusable (R) for that sample. However, qualification of the data is left up to the professional judgment of the reviewer. Discuss any action below:

Calibration

Date of initial calibration:_____
Date(s) of associated continuing calibrations:_____
Instrument ID:_____

List all congeners that have %RSCEs that exceed 15% or %Ds that exceed 25%. (Use additional sheets if necessary.)

Date/Time	Column	%RSCE or %D	Compound (value)	Samples Affected

Action: If %RSCE > 15% or %D > 25%, but ≤ 50%, qualify all positive results as estimated (G).

If %RSCE or %D > 50%, quality all positive and nondetect results as estimated (G, UG).

Were the correlation coefficients for each PCB congener and surrogate ≥ 0.995? ☐ yes ☐ no

Was the correct analytical sequence followed? ☐ yes ☐ no

Were all samples analyzed within 12 hours of a calibration standard? ☐ yes ☐ no

If no, list affected samples and discuss any actions:

_____
_____
_____

Blanks

List on the blank contamination worksheet all confirmed and unconfirmed blank contaminants detected in the method, field, and instrument blanks that are ≥ 0.1 ppb in extract. Based upon the highest concentration of contaminant in any blank (x), establish action levels of 5x. (Use additional sheets if necessary.)

Congener	Maximum Concentration (ppb in extract)	Action Level (ppb in extract)	CRQL

Action: Qualify any positive results < action level as also detected in associated blank (B).

Blank Contamination Worksheet

Page of

Congener						
BZ#1						
BZ#2						
BZ#3						
BZ#4						
BZ#5						
BZ#6						
BZ#7						
BZ#8						
BZ#9						
BZ#10						
BZ#12						
BZ#15						
BZ#16						
BZ#18						
BZ#19						
BZ#22						
BZ#25						
BZ#26						
BZ#27						
BZ#28						
BZ#29						
BZ#31						
BZ#37 (with BZ#59)						
BZ#40						
BZ#41						
BZ#44						
BZ#47						
BZ#49						
BZ#52						
BZ#53						
BZ#56						
BZ#66						
BZ#70						
BZ#75						
BZ#77						
BZ#82						
BZ#83						
BZ#84						
BZ#85						
BZ#87						
BZ#91						
BZ#92						
BZ#95						
BZ#97						
BZ#99						
BZ#101						
BZ#105						
BZ#107						
Associated Samples						

Congener						
BZ#115						
BZ#118						
BZ#119						
BZ#122						
BZ#123						
BZ#126						
BZ#128						
BZ#129						
BZ#136						
BZ#137						
BZ#138						
BZ#141						
BZ#148						
BZ#151						
BZ#153						
BZ#157						
BZ#158						
BZ#167						
BZ#170						
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BZ#193						
BZ#194						
BZ#195						
BZ#196						
BZ#198						
BZ#199						
BZ#200						
BZ#201						
BZ#202						
BZ#205						
BZ#206						
BZ#207						
BZ#208						
BZ#209						
Associated Samples						

Surrogate Spike Recoveries

List the samples which did not meet the surrogate recovery criteria of 60-150%.

Sample ID	TCMX % Recovery	OCN % Recovery

Actions: If the TCMX recovery is outside control limits, qualify positive and nondetect results as estimated (G, UG).

If the TCMX recovery is below 10%, qualify positive results as estimated (G) and nondetect results as unusable (R). Sample requires reextraction and reanalysis. Identify reextractions and reanalyses by adding an "RE" suffix to the sample ID.

Matrix Spike/Matrix Spike Duplicate (Section 1)

List the percent recoveries and RPDs of compounds which did not meet the percent recovery criteria of 60-150% or the RPD criteria of 40%.

Sample ID	PCB Congener	% REC/RPD

Qualification is limited to the unspiked sample only.

Action: If any compound does not meet the percent recovery criteria, quality positive results as estimated (G). If any compound recovery is below 10%, qualify positive results as estimated (G) and nondetect results as unusable (R).

If any compound does not meet the RPD criteria, qualify positive results of that compound as estimated (G).

As separate worksheet should be used for each MS/MSD pair.

Matrix Spike/Matrix Spike Duplicate (Section 2)

Sample Nos.:_____

List the concentrations of the nonspiked congeners in the sample, matrix spike, and matrix spike duplicates, which are ≥ CQL, and which did not meet the %RSD criteria of 40% RSD.

Congener	Sample, MS, MSD Concentrations	% RSD

Action: Any nonspiked congeners that have a %RSD > 40% should be estimated (G) in the nonspike sample. If a congener is reported in the MS and/or MSD at a concentration ≥ CQL but is not detected in the sample, estimate the nondetect result (UG).

Matrix Spike Blank

List the percent recoveries of congeners which did not meet the percent recovery criteria of 60-150%.

PCB Congener	% REC

No action is taken based on matrix spike blank results.

Field Duplicate Precision

Sample Nos.:_____

List the concentrations of the compounds, which are ≥ CQL, and which did not meet the RPD criteria of < 50%.

Compound	Sample Conc.	Dup. Sample Conc.	RPD

Action: If the results for any compounds do not meet the RPD criteria, qualify the positive results for that congener as estimated.

If one value is nondetect, and one is ≥ CQL, qualify the positive and nondetect results as estimated (G, UG).

A separate worksheet should be used for each field duplicate pair.

Compound Identifications

List the reported results which have RTs that fall outside of the established RTWs.

Sample ID	PCB Congener	RT	RTW

Compound Quantitation

List the GC/ITD and GC/ECD PCB congener results which exceed 50% RPD and are at sufficient concentration to be detected by GC/ITD. (Use additional sheets if necessary.)

Sample ID	PCB Congener	GC/ECD result (ppb)	GC/ITD result (ppb)	RPD

Action: If RPD > 50%, estimate (G) positive results.

If GC/ECD result with a concentration within GC/ITD calibration range is not confirmed by GC/ITD, qualify (Q).

If GC/ITD result was not detected by GC/ECD, or greater than 5 times GC/ECD result, qualify (M).

Performance Evaluation Sample

List the GC/ECD results for the performance evaluation sample along with the known concentration and advisory range.

PCB Congener	Result (ppb)	Known Concentration (ppb)	Advisory Range (ppb)

No action is taken during validation based on the performance evaluation data.

Appendix A-7
Standard Operating Procedures Data Validation for Congener Specific Detemrination of Polychlorinated Biphenyls (PCBs) by Gas Chromatography/Ion Trap Detector (GC/ITD)

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Appendix A-7

STANDARD OPERATING PROCEDURES DATA VALIDATION FOR CONGENER SPECIFIC DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY/ION TRAP DETECTOR (GC/ITD)

METHOD SUMMARY

The analytical methods described the Appendices of the Sampling and Analysis Plan/Quality Assurance Project Plan (SAP/QAPjP) for the Hudson River PCB Reassessment RI/FS are extraction, cleanup,and analytical methods for PCB congeners. Briefly, the polychlorinated biphenyl (PCB) congeners are extracted from water, sediment, particulate (filter), and biota samples. The resulting hexane extracts are processed through various cleanup procedures, and then are analyzed by fused silica capillary column gas chromatography with electron capture detector (GC/ECD). The PCBs are identified and quantitated by congener. A subset of the sample extracts (approximately 5 to 10% of the samples, as specified in the SAP/QAPjP), as well as any Performance Evaluation (PE) samples, will be analyzed to confirm the congener identification by gas chromatography/ion trap detector (GC/ITD). The GC/ITD analyses will also provide quantitative confirmation of the congeners. This standard operating procedure (SOP) details the process of validation for samples analyzed for congener specific determination of PCBs by GC/ITD. The data validation SOP for the GC/ECD analyses are provided in Appendix A-6.

I. DATA COMPLETENESS

The data deliverables for these methods will include, at a minimum:

- Case narrative
- Chain-of-Custody records
- Sample results summaries (Form I or equivalent)
- Retention time window summaries
- Initial and continuing calibration summaries (Form VI and VII or equivalents)
- Raw data for each field sample and quality control (QC) sample, including chromatograms, quantitation reports, and sample preparation logbook summaries
- Ion Trap Detector tuning (DFTPP) summaries (Form V or equivalent) and raw data, including mass list and mass spectra
- GC/ITD calibration summaries, including raw data and selected ion current profiles (SICPs)
- GC/ITD data for each confirmed sample, including SICPs and quantitation reports

The specific sample weight, final volume, and cleanup procedures used for each sample should be clearly identified in the data.

The GC/ITD results will be used primarily to confirm the GC/ECD PCB congener identifications, with quantitative verification of the GC/ECD results as a secondary goal. Matrix spike and laboratory spiked blank samples will not be analyzed by GC/ITD. Therefore, there are no data validation requirements for these quality control parameters.

II. HOLDING TIMES

A. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from time of collection to time of sample preparation or analysis, as appropriate.

B. Criteria

Both samples and extracts must be preserved at 4° C. Water, sediment, and particulate samples must be extracted within 7 days of sample collection and the extract must be analyzed within 40 days following extraction, according to EPA's "Laboratory Data Validation Functional Guidelines for Evaluating Organic Analysis" (February 1, 1988) and EPA Region II's "SOP No. HW-6, Revision 8" (January, 1992).

C. Evaluation Procedure

Holding times are calculated by comparing the sampling date on the EPA SAS Packing List/Chain-of-Custody records with dates of extraction and analysis listed on the Form I (or equivalent).

D. Action

If the holding times are exceeded, flag all positive and nondetect results as estimated (G and UG, respectively) and document in the validation report that holding times were exceeded. If the extraction or analytical holding times are grossly exceeded (i.e., by more than 14 days), either upon initial analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data. The reviewer may determine that the nondetect data are unusable (R).

III. GC/ITD TUNING

A. Objective

Decafluorotriphenylphosphine (DFTPP) tuning and performance criteria are established to ensure mass resolution, identification, and sensitivity. These criteria are derived from EPA Method 525 (a GC/ITD method). The criteria are not sample specific; conformance is determined using standard materials. Therefore, these criteria should be met in all circumstances.

B. **Criteria**

The ion abundances presented in Table 5 of Appendix A-5 must be achieved.

C. **Evaluation Procedure**

1. Verify from the raw data that the mass calibration is correct.

2. Compare the data presented on each GC/ITD Tuning and Mass Calibration Form (Form V or equivalent) with each mass listing submitted.

3. Ensure the following:

   a. Verify that the Form V (or equivalent) is present for each 12-hour period.

   b. The laboratory has not made any transcription errors.

   c. The appropriate number of significant figures has been reported.

   d. The laboratory has not made any calculation errors.

4. If possible, verify that spectra were generated using appropriate subtraction techniques. Since the DFTPP spectra are obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions.

D. **Action**

1. If the mass calibration is in error, qualify all data as unusable (R).

2. If the ion abundances are not met, professional judgment may be applied to determine to what extent the data may be utilized. The reviewer should refer to EPA's "Laboratory Data Validation Functional Guidelines for Evaluating Organic Analyses" (February 1, 1988) and EPA Region II's "SOP No. HW-6, Revision 8" (January, 1992) for additional guidance.

IV. INSTRUMENT PERFORMANCE

A. **Objective**

Instrument performance criteria are established to ensure that adequate chromatographic resolution is achieved, which is crucial for qualitative identification of the congeners. These are method criteria and therefore all criteria should be met in all circumstances.

B. **Criteria**

1. Resolution Check

There should be baseline separation of PCB congener BZ#87 from PCB congeners BZ#154 and BZ#77 (which may coelute). When these criteria cannot be met, quantitation may be adversely affected because of the difficulty in establishing a baseline.

2. Ion Trap Detector Sensitivity

The signal/noise ratio for m/z 499 of PCB congener BZ#209 and for m/z 241 of chrysene-d_{12} must be ≥ 5.

3. Ion Trap Detector Calibration

The abundance of m/z 500 relative to m/z 498 for PCB congener BZ#209 (C_{10}-PCB) should be $\geq 70\%$ but $\leq 95\%$.

C. **Evaluation Procedure**

1. Check the raw data to verify that there is baseline resolution of BZ#87 from BZ#154 and BZ#77. Note any other congener pairs that have resolutions less than 75%.

$$\%\ Resolution = \frac{height\ of\ smaller\ peak - height\ of\ valley\ separating\ peaks}{height\ of\ smaller\ peak} \times 100\%$$

2. Check the raw data to verify that the signal/noise ratio for m/z 499 of PCB congener BZ#209 and for m/z 241 of chrysene-d_{12} is ≥ 5.

3. Check the raw data to verify that the abundance of m/z 500 relative to m/z 498 for PCB congener BZ#209 (Cl_{10}-PCB) is $\geq 70\%$ but $\leq 95\%$.

D. **Action**

1. If BZ#87 is not resolved from BZ#154 and BZ#77, a close examination of the chromatography is necessary to ensure adequate separation of the congeners. If adequate separation ($>75\%$) of any congener pair is not achieved, the reviewer may use professional judgment to estimate (G) the positive congeners results for a poorly resolved pair if there is sufficient evidence that the congeners are present in the sample. The SICPs should also be reviewed to confirm the level of chlorination in each unresolved congener pair.

2. If the signal/noise ratio criteria for m/z 499 of PCB congener BZ#209 and for m/z 241 of chrysene-d_{12} is not achieved, qualify the nondetect sample results as unusable (R).

3. If the abundance of m/z 500 relative to m/z 498 for PCB congener BZ#209 is not achieved, qualify the positive and nondetect sample results as estimated (G and UG, respectively). The reviewer may use professional judgment to qualify nondetect results as unusable (R).

4. Relative retention times are used in qualitative identification. Significant RRT shifts in the calibration standards should be carefully evaluated. Qualification of the data is left up to the professional judgment of the data reviewer.

V. CALIBRATION

A. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance prior to the analysis of samples, and the continuing calibration checks document satisfactory maintenance and adjustment of the instrument over a specific time period.

B. Criteria

1. Initial Calibration

The Percent Relative Standard Deviation (%RSD) of the congener relative response factors (RRF) must not exceed 20%.

$$RRF = A_x Q_{is} / A_{is} Q_x$$

where,

A_x = integrated ion abundance of quantitation ion for a PCB calibration congener

Q_{is} = integrated ion abundance of m/z 240, the quantitation ion when chrysene-d_{12} is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-d_{10} is used as the internal standard

A_{is} = injected quantity of chrysene-d_{12} or phenanthrene-d_{10}

Q_x = injected quantity of PCB congener

RRF = relative response factor is a unitless number; therefore, units used to express all quantities in the equation must be equivalent

$$\% \ RSD = \frac{SD}{\overline{RRF}} \times 100\%$$

where,

SD = Standard Deviation of the calibration factors

$\overline{RRF}$ = Mean Relative Response Factor

2. Continuing Calibration

A mass spectrometer tune and continuing calibration check must be performed for each 12-hour period during which analyses are performed. The relative response factor for each congener must be within 20% of the mean calibration factor from the five-level calibration at the beginning and end of the sequence.

$$\% \ D = \frac{\overline{RRF_I} - RRF_s}{\overline{RRF_I}} \times 100\%$$

where,

$\overline{RRF_I}$ = Mean relative response factor from initial calibration

RRF_s = Relative response factor from continuing standard

C. **Evaluation Procedure**

1. Inspect the initial calibration summary forms and verify agreement with the raw data. Recalculate 10% of the data to verify the reported %RSDs. If errors are detected, a more comprehensive recalculation must be performed.

2. Inspect the continuing calibration summary form and verify agreement with the raw data. Recalculate 10% of the data to verify the reported percent difference (%D), using the following formula. If errors are detected, a more comprehensive recalculation must be performed.

D. **Action**

1. If the criteria for linearity are not met (%RSD and %D), flag all associated quantitated results as estimated (G).

2. If the %D between the continuing relative response factor and the mean relative response factor of a congener is greater than 20%, flag associated positive sample results as estimated (G) for that congener. If the %D grossly exceeds 20%, the reviewer should use professional judgment to determine the extent and direction of the bias, and estimate the nondetect results if deemed necessary. If, in the opinion of the reviewer, the variability in instrument response is so great that all positive and nondetect results are suspect, the data may be unusable (R).

   The reviewer must carefully document the qualification of data, with detailed descriptions of potential biases.

VI. INTERNAL STANDARD PERFORMANCE

A. Objective

Internal Standards (IS) performance criteria ensure that GC/ITD sensitivity and response are stable during every run.

B. Criteria

1. The IS area counts must not vary by more than 30% from the most recent calibration or by more than 50% from the initial calibration.

2. The absolute retention time of the IS must be within 10 seconds of the retention time in the most recent calibration.

3. For chrysene-d_{12}, the abundance of m/z 241 relative to m/z 240 must be $\geq$ 15% and $\leq$ 25%, and these ions must maximize simultaneously. For phenanthrene-d_{10}, the abundance of m/z 189 relative to m/z 188 must be $\geq$ 10% and $\leq$ 22%, and these ions must maximize simultaneously.

C. Evaluation Procedure

1. Check the raw data to verify the recoveries reported on the IS area summary form (Form VIII or equivalent).

2. Verify that all retention times and IS areas are acceptable.

3. Verify that the ion ratios are acceptable.

D. Action

1. If the area count is outside of the 30% criterion (or the 50%, if applicable),

   a. Positive results for the congeners quantitated relative to that IS are flagged as estimated (G).

   b. Nondetects for congeners quantitated using that IS are flagged with the sample quantitation limit classified as estimated (UG).

c. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. Nondetects should then be flagged as unusable (R).

2. If the absolute IS retention time varies by more than 10 seconds, the reviewer must determine if false positives or false negative exists due to the shift. Qualification of the data is left up to the professional judgment of the data reviewer.

3. If the ion ratios criteria are not met, the reviewer should determine if the problem is due to interferences that are present or if there has been a significant change in the mass spectrometer tuning. If an interferant is present for one of the IS, the reviewer should determine if the other IS is unaffected, and recalculate the affected congener concentrations. If tuning problems are indicated, the reviewer should carefully review the SICPs for each congener to determine if meaningful results can be extracted from the data. The reviewer should estimate (G) any results which may be usable, or reject (R) results which are unusable.

VII. COMPOUND IDENTIFICATION

A. Objective

Qualitative criteria for compound identification have been established to minimize the number of erroneous identifications of congeners. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). For this project, the primary goal is to confirm the presence or absence of specific PCB congeners. Some congeners may have been detected by GC/ECD but will not be detectable by GC/ITD, due to insufficient concentrations.

B. Criteria

1. The relative retention time (RRT) of a reported congener must be within $\pm$ 0.06 RRT units of the standard RRT.

2. The quantitation and confirmation ions must maximize within $\pm$ 1 scan of each other.

3. The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

4. The ratio of the quantitation ion area to the confirmation ion area must be within the limits found in Table 7 of Appendix A-5, and at least one ion in the $(M-70)^+$ ion cluster must be present.

C. Evaluation Procedure

1. Review the reported RRT results and the associated raw data (chromatograms and data system printouts). Confirm the reported positive detects, using appropriate RRT data, and verify that the congeners listed as "not detected" (nondetects) are correct.

2. Review the SICPs and verify that the quantitation and confirmation ion currents maximize within ± 1 second of each other.

3. Verify the signal-to-noise ratio for each positive and nondetect result. Verify that the detector has not been saturated. Detector saturation is often discernible as a "flattened" (non-Gaussian) peak or by a sudden drop of the ion current signal-to-baseline due to the overload protection devices on most electron multipliers.

4. Review the SICPs and quantitation reports to verify that the proper ion ratios were found.

D. **Action**

If the qualitative criteria for compound identification are not met, all reported positive results should be considered nondetects. The reviewer should use professional judgment to assign an appropriate quantitation limit. If the misidentified peak poses an interference with potential detection of a target congener, then the reported value should be considered and flagged as an estimated nondetected result at the appropriate quantitation limit (UG). The reviewer should be aware of potential interferences identified in the GC/ECD analyses and determine what impact the interferences may have on the data.

VIII. COMPOUND QUANTITATION

A. **Objective**

The objective is to ensure that the reported quantitation results are accurate.

B. **Criteria**

Compound quantitation must be calculated according to the following calculation:

$$C_x = (A_x \cdot Q_{is}) / (A_{is} \cdot RF \cdot W)$$

where C_x = concentration (µg/kg or µg/L) of surrogate compound, a PCB isomer group, or an individual PCB congener.

A_x = the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination, or the quantitation ion area for one PCB congener or surrogate compound.

A_{is} = the area of the internal standard quantitation ion, m/z 240 for chrysene-d_{12} or m/z 188 for phenanthrene-d_{10}.

Q_{is} = quantity (µg) of internal standard added to the extract before GC/ITD analysis.

RF = calculated response factor for the surrogate compound or the PCB calibration compound for the isomer group (level of chlorination).

W = dry weight (kg) or volume (L) of sample extracted.

C. **Evaluation Procedure**

1. Raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation reports, SICPs, and sample preparation log sheets should be compared to the reported positive results.

2. Verify that congeners detected in the sample extracts analyzed by GC/ECD, at sufficient concentration to be analyzed by GC/ITD are detected. The GC/ITD congener calibration ranges are summarized below:

BZ#1 through #39	10 ppb to 500 ppb in extract
BZ#40 through #169	20 ppb to 1000 ppb in extract
BZ#170 through #205	30 ppb to 1500 ppb in extract
BZ#206 through #209	50 ppb to 2500 ppb in extract

3. Verify that the GC/ITD congener results are within 50% RPD of those from the GC/ECD analyses.

D. **Action**

If incorrect results or quantitation limits have been reported by the laboratory, the reviewer should contact the laboratory and request resubmittals of all affected data.

Quantitation limits affected by large peaks should be flagged as unusable (R). The reviewer may also elect to provide an estimated detection limit for the affected congeners.

If the RPD between the GC/ECD and GC/ITD analyses exceeds 50% for a given congener, the positive result should be estimated (G). If the congener was detected in the sample extract by GC/ECD at sufficient concentration to be analyzed by GC/ITD, but is not found during the GC/ITD analysis, the positive GC/ECD results should be qualified as not confirmed by GC/ITD (Q). If the congener was detected in the sample extract by GC/ITD analysis, but was not detected by GC/ECD or was detected at a significantly lower concentration (< 1/5 of the GC/ITD value), then the positive or nondetect GC/ECD result should be qualified as (M). The reviewer should also examine the GC/ECD chromatogram to determine if the congener may have been misidentified due to two or more congeners within one domain or if the peak was obscured by a large positive interference. Discuss any finding in the validation narrative.

IX. PERFORMANCE EVALUATION SAMPLES

A. **Objective**

The performance evaluation samples are analyzed to determine accuracy of the analytical method as performed by the laboratory. These data will not be used to qualify the results of individual

samples but will be assessed as an indicator of overall laboratory performance of the method in the usability assessment.

B. **Criteria**

The advisory limits for PCB congener concentrations will be provided with the performance evaluation sample by the vendor.

C. **Evaluation Procedure**

Verify the reported results and calculations by reviewing the raw data.

D. **Action**

No action is taken during validation based on the performance evalution data. However, during the data usability assessment, the reviewer will use this information in conjunction with other QC criteria to determine the need for qualification of the data.

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Validation Worksheets
for PCB Congeners by GC/ITD

Laboratory:_____ Site: Hudson River PCB site

Case no.:_____ SDG no.:_____

Sampling date(s):_____ Number of samples:_____

Matrix:_____ Shipping date:_____

Date received by laboratory:_____

Sample IDs:_____

The general criteria used to determine the quality of the data were based on the examination of:

- Data completeness
- Holding times
- GC/ITD tuning
- Instrument performance
- Calibration
- Internal standard performance
- Compound identification
- Compound quantitation
- Performance evaluation sample

Data validation was performed following the guidelines in "Data Validation Guidelines for Congener Specific Determination of Polychlorinated Biphenyls (PCBs) by Gas Chromatography/Ion Trap Detector (GC/ITD)," Appendix A-7, SAP/QAPjP for the Hudson River PCB Reassessment RI/FS, January 1993.

Overall Comments:_____

Definitions and qualifiers:

U - Not detected
J - Compound detected below calibration range
G - Estimated data due to quality control criteria
R - Reject data due to major exceedance of quality control criteria
M - Positive GC/ITD result was not detected by GC/ECD analysis or greater than 5 times GC/ECD result.
Q - GC/ECD result at concentration within GC/ITD calibration range, but not confirmed by GC/ITD analysis.

Primary Reviewer:_____ Date:_____

Senior Reviewer:_____ Date:_____

Data Completeness

Missing Information	Date Lab Contacted	Date Received

Holding Times

List all samples that exceeded the extraction holding time of 7 days from sample collection or the analysis holding time of 40 days following extraction.

Sample ID	Date Sampled	Date Extracted/ # of Days	Date Analyzed/ # of Days

Action: Qualify the positive and nondetect results as estimated (G, UG).

GC/ITD Tuning

The DFTPP performance results were reviewed and found to be within the criteria specified in Appendix A-5.

If no, list samples affected and associated tune.

Sample ID	Date/Time of Analysis	DFTPP Date/Time of Analysis	Outlier

Action: If the mass calibration is in error, classify all data as unusable (R).

If the ion abundances are not met, professional judgment may be applied to determine what extent the data may be utilized.

List any samples analyzed greater than 12 hours after the preceding DFTPP tune.

Sample ID	Date/Time of Analysis	DFTPP Date/Time of Analysis

Action: Qualify positive and nondetect results as estimated (G, UG).

Instrument Performance

_____ Resolution check - Baseline separation of PCB congener BZ#87 from PCB congeners BZ#154 and BZ#77 (which may coelute) has been achieved.

If no, list samples affected:_____

List any PCB congener pairs that have not met adequate separation (>75%):

PCB Congener	% Resolution

Action: The reviewer may use professional judgment, based on the chromatography review, to estimate (G) the positive congener results for a poorly resolved pair(s).

_____ Ion trap detector sensitivity - The signal/noise ratio for m/z 499 of PCB congener BZ#209 and for m/z 241 of chrysene-d_{12} is ≥5?

If no, list affected samples:_____

Action: Qualify the nondetect sample results as estimated (UG).

_____ Ion trap detector calibration - The abundance of m/z 500 relative to m/z 498 for PCB congener BZ#209 is ≥70% but ≤95%?

If no, list affected samples:_____

Action: Qualify the nondetect and positive sample results as estimated (G, UG).

Calibration

Date of initial calibration:_____
Date(s) of associated continuing calibrations:_____
Instrument ID:_____

List all congeners that have %RSDs or %Ds that exceed 20%. (Use additional sheets if necessary.)

Date	%RSD or % D	Compound (value)	Samples Affected

Action: If %RSD or %D, >20% but ≤50%, qualify all positive results are estimated (G).

If %RSD or %D, >50%, quality all positive and nondetect results are estimated (G, UG).

Internal Standard Performance

Internal Standard Areas

List the internal standard (IS) areas of samples which did not meet the criteria of ±30% of the areas in the most recent continuing calibration standard or ±50% of the areas in the initial calibration midpoint standard.

Sample ID	Date	IS	IS Area	CCAL or ICAL IS area	%D

Action: Qualify positive and nondetect results associated with internal standard as estimated (G, UG). If extremely low area counts are reported nondetect results should be qualified as unusable (R).

Internal Standard Retention Times

List the internal standard retention times of samples which did not meet the criteria of ±10 seconds of the internal standards in the most recent calibration standard.

Sample ID	Date	IS	IS RT	CCAL RT	Δ Sec

Action: The reviewer must determine if false positive or false negatives exist due to retention time shifts. Qualification of the data is left up to the reviewer's professional judgment.

Internal Standard Performance (cont.)

Internal Standard Ion Ratios

List the internal standard ions ratios which did not meet the following criteria in samples:

The abundance of m/z 189 relative to m/z 188 for phenanthrene-d_{10} must be $\geq 10\%$ and $\leq 22\%$ and these ions must maximize simultaneously. The abundance of m/z 241 relative to m/z 240 for chrysene-d_{12} must be $\geq 15\%$ and $\leq 25\%$ and the ions must maximize simultaneously.

Sample ID	Date	IS	IS ion ratio

Action: The reviewer should determine if the problem is due to interferences or a significant change in mass spectrometer tuning. If an interference is present and the other IS is unaffected recalculate the affected PCB congener concentrations using the unaffected IS. If tuning problems are indicated, the reviewer should review the SICPs for each congener to determine if meaningful results can be extracted from the data. Estimate usable results (G) and reject (R) results which are unusable.

Compound Identification

Relative Retention Time

List the reported results which did not meet the RRT criteria of ± 0.06 RRT units from the standard RRT.

Sample ID	PCB Congener	RRT - Sample	RRT - Standard	Δ RRT

Signal/Noise

List the reported results which did not meet the signal/noise ion criteria of > 3.

Sample ID	PCB Congener	Signal/Noise Ratio

Compound Identification (cont.)

Quantitation and Confirmation Ion Retention Times

List the reported results in which the quantitation and confirmation ions did not maximize within ±1 scan.

Sample ID	PCB Congener

Ion Ratio

List the reported results which did not meet the ion ratio criteria found in Table 7 of Appendix A-5.

Sample ID	PCB Congener	Ion Ratio	Ion Ratio Limit

Action: If any of the above criteria are not met, qualify the results as nondetect and estimated at the quantitation limit (UG).

Compound Quantitation

List the GC/ITD and GC/ECD PCB congener results which exceed 50% RPD and are at sufficient concentration to be detected by GC/ITD. (Use additional sheets if necessary.)

Sample ID	PCB Congener	GC/ECD result (ppb)	GC/ITD result (ppb)	RPD

Action: If RPD >50%, estimate (G) positive results.

If GC/ECD result, with a concentration within GC/ITD calibration range, is not confirmed by GC/ITD, qualify (Q).

If GC/ITD result was not detected by GC/ECD or greater than 5 times GC/ECD result, qualify (M).

Performance Evaluation Sample

List the GC/ITD results for the performance evaluation sample along with the known concentration and advisory range.

PCB Congener	Result (ppb)	Known Concentration (ppb)	Advisory Range (ppb)

No action is taken during validation based on the performance evaluation data.

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Appendix A-8
Extraction and Cleanup of Benthic Invertebrate Samples for PCB Congener Analysis and Determination of Lipid Content of Extracts

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Appendix A-8

EXTRACTION AND CLEANUP OF INVERTEBRATE TISSUE SAMPLES FOR PCB CONGENER ANALYSIS AND DETERMINATION OF LIPID CONTENT OF EXTRACTS

1.0 Scope and Application

1.1 This is a procedure for the extraction and cleanup of polychlorinated biphenyls (PCBs) from river invertebrate tissue samples. The procedure is based on the extraction procedure of Bush, Streeter, and Sloan (1989) and EPA method 3620A (Florisil cleanup). The extract is suitable for determination of total extractable lipids.

1.2 This extraction and cleanup procedure is meant to be followed by determination of congener specific PCB per analysis by Gas Chromatography - Electron Capture Detector (GC/ECD) analysis.

2.0 Summary of Method

2.1 A subsample of the ground tissue is mixed with anhydrous sodium sulfate to dryness, placed in a Tekmar tissuemizer, extracted with hexane, and then concentrated.

2.2 The concentrated extract is applied to an activated Florisil column and eluted with hexane to reduce the matrix interferences caused by polar compounds.

2.3 The eluate from the Florisil column cleanup is concentrated once again using a K-D apparatus and the final extract volume is adjusted to 1 ml.

2.4 The final extract is suitable for gas chromatographic analysis.

2.5 The initial extract, prior to concentration and cleanup, is suitable for determination of total extractable lipids by evaporation of the solvent.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware that lead to false positive peaks and/or elevated baselines in gas chromatograms. All of the reagents and glassware used must be routinely demonstrated to be free from interferences (contaminants) under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in PCB congener analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broadly eluting peaks. Common, flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of all plastics, except Teflon, in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination once it becomes a problem.

3.2 To minimize interferences from contamination, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry, dry in a 100°C oven or, if necessary, heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. (Volumetric glassware should not be heated in a muffle furnace because the calibrated volume may be affected.)

4.0 Apparatus and Materials

4.1 Tekmar (Cincinnati, Ohio) tissuemizer - Equipped with 1/4 inch blade.

4.2 Kuderna-Danish (K-D) apparatus.

4.2.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation Flask - 250 ml (Kontes K-5700-1-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column - Three-ball macro (Kontes K-503000-121 or equivalent).

4.2.4 Snyder column - Two-ball micro (Kontes K-569001-219 or equivalent).

4.2.5 Concentrator tube - 25 ml, graduated (Kontes 569355-0000 or equivalent).

4.2.6 Snyder column - 3 chamber (Kontes 570050-2526 or equivalent).

4.3 Boiling Chips - Silicon carbide or equivalent, approximately 10/40 mesh, solvent extracted with hexane for approximately one hour and heated to 400°C for 30 minutes.

4.4 Water Bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a fume hood.

4.5 Vials - Amber glass 2 ml, and clear glass 7 ml and 20 ml capacities, with Teflon-lined screw caps.

4.6 Disposable glass pasteur pipet and bulb.

4.7 Balance - Analytical, calibrated with S-class weights, capable of accurately weighing ± 0.01 mg.

4.8 Apparatus for Florisil Column cleanup procedure.

4.8.1 Glass chromatographic column, 20-mm ID with Teflon stopcock and reservoir.

4.8.2 Erlenmeyer flask (250 ml).

4.8.3 Glass stoppers.

4.8.4 Long glass rod.

4.8.5 Glass wool - Rinsed with hexane and dried before use.

4.9 Drying Oven

4.10 Dessicator

4.11 Aluminum weighing pans

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 reducing the accuracy of the determination due to the introduction of contaminants.

5.2 ASTM Type II Water (ASTM D-1193-77) or equivalent. All references to reagent water in this method refer to ASTM Type II unless otherwise specified.

5.3 Sodium sulfate (granular, anhydrous) - Purification is by washing with hexane followed by heating at 400°C for four hours in a shallow tray.

5.4 Hexane - Pesticide quality or equivalent.

5.5 PCB Surrogate Standard Spiking Solution.

5.5.1 The surrogate standards are added to all samples, blanks, and matrix spikes prior to extraction. The surrogate compounds are tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN).

5.5.2 Prepare the surrogate standard spiking solution at a concentration of 0.2 µg/1.00 ml of each of the two compounds in hexane. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers and protect from light. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicates a problem. **CAUTION**: Analysts must allow all spiking solutions to equilibrate to room temperature before use.

5.6 PCB Congener Matrix Standard Spiking Solution.

5.6.1 Prepare a matrix spike standard solution that contains each of the congeners listed in Table 1 in hexane. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers and protect from light. Stock solutions must be replaced after twelve months, or sooner if comparison with check standards indicates a problem. **Caution**: Each time a vial is warmed to room temperature and opened, a small

volume of solvent in the vial headspace evaporates, significantly affecting concentration. Solutions should be stored with the smallest possible headspace, and opening vials should be minimized. Analyst must allow all spiking solutions to equilibrate to room temperature before use.

5.6.2 Matrix spikes are also to serve as duplicates by spiking two equal aliquots from the one sample chosen for spiking (i.e., matrix spike and matrix spike duplicate samples).

5.7 Florisil - Pesticide residue (PR) grade (60/100 mesh). Purchase activated at 1250°F (677°C), stored in glass containers with ground glass stoppers or foil-lined screw caps.

5.7.1 Deactivation of Florisil - Just before use, weigh out 1000 g of Florisil into a glass container and heat at 130°C for 16 hours. After heating, cool in a desiccator. Pour into a 4-L solvent bottle, close with a Teflon-lined cap and place on a tumbler or roller. Dropwise add 40 ml of water while shaking to deactivate. Tumble for at least 4 hours. There should be no lumps present. Store in a tightly closed amber bottle. Let stand overnight before using.

5.7.2 Florisil activity check - Before each batch of Florisil is first used, and once a week thereafter, test the Florisil by adding 1 ml of GC/ECD CAL STD-3 and following procedures in section 7.11. All resolvable PCB congeners should be present in the extract after column elution. The recovery of the resolvable PCB congeners must be determined for evaluation purposes. The lot of Florisil cartridges is acceptable for use if the PCB congeners are within the range of 60% to 150%. Some batches of Florisil may require 4% deactivation to allow all PCB congeners to be eluted by 50 ml of hexane.

6.0 Sample Collection, Preservation and Handling

6.1 Sample collection is in accordance with the procedures specified in Section 6 of the SAP/QAPjP.

6.2 Preservation - The laboratory must record the temperature of the shipping containers (coolers) upon receipt. In the laboratory and prior to extraction, all samples must be kept frozen in a freezer storage unit at a temperature below 0°C.

6.3 Holding Time - Extraction of samples must be initiated within 5 days of verified time of sample receipt (VTSR) and extracts analyzed within 40 days following extraction.

7.0 Extraction and Cleanup Procedure

7.1 For invertebrate tissue samples, grind the sample (approximately 1 g) to a fine paste using a Tekmar tissuemizer equipped with a 1/4 inch blade.

7.2 Reblend the sample with 2 g of anhydrous sodium sulfate to remove water from the sample. The sodium sulfate should be added in small aliquots. Add 1.0 ml of 0.2 μg/ml surrogate standard spiking solution into the sample. For the sample in each analytical batch selected for congener spiking, add 1.0 ml of 0.2 μg/ml matrix spike standard solution. The surrogate and matrix spiking procedures must be witnessed by another analyst, and verified on the extraction log.

7.3 Extract the sample with 10 ml of hexane in the tissuemizer for a period of one minute.

7.4 Quantitatively transfer the resulting extract to a 250-ml K-D evaporation flask.

7.5 Repeat the extraction twice using a 10-ml aliquot of hexane each time and combine the hexane phases in the K-D evaporation flask.

7.6 If the determination of lipid content is to be performed on the extract, record the extact volume of the combined extract (to two significant figures) and transfer a meaured volume (to two significant figures) of approximately 5 ml of the combined extract to an aluminum weighing pan (see section 8.0).

7.7 Assemble the K-D concentrator by attaching a 10-ml concentrator tube to the 250-ml evaporation flask.

7.8 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding 1.0 ml of hexane 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 hot water temperature, as required, to complete the concentration in 10 to 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 has

reached 1 to 2 ml, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE K-D TUBE TO GO DRY.

7.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 to 2 ml of hexane.

7.10 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in the calibration solutions. Nitrogen blow-down is not allowed since its employment may result in intermittent loss of the more volatile PCB congeners.

7.11 The concentrated extract may now be further cleaned on an activated Florisil column. If the cleanup of the extract will not be performed immediately, transfer the concentrate, using a pasteur pipet, to a 7-ml Teflon-lined, screw-cap vial (rinsing concentrator tube with several aliquots of hexane into the vial) and store refrigerated.

7.12 Florisil Column Cleanup.

7.12.1 Florisil Column Preparation - Fill the chromatography column to about two-thirds full with hexane. Add a piece of glass wool to the bottom of the column with the help of a long glass rod. Remove any air bubbles which become trapped in the glass wool. Add 20 g of the deactivated Florisil to a 20-mm ID chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate. DO NOT LET SODIUM SULFATE BECOME EXPOSED TO AIR.

7.12.2 Transfer the sample extract from the K-D concentrator tube or vial to the Florisil column. Rinse the tube twice with 1 to 2 ml hexane, adding each rinse to the column.

7.12.3 Place a 250-ml erlenmeyer or round-bottom flask under the chromatographic column. Drain the column into the flask until the sodium sulfate is nearly exposed. Elute the column with 55 ml of hexane. Elute at a 5 ml/min rate. Collect the first 40 ml of the eluate. DO NOT LET GRANULAR SODIUM SULFATE BECOME EXPOSED TO AIR.

7.12.4 The eluate is then concentrated with the K-D apparatus to an apparent volume of 1 ml for gas chromatographic analysis. DO NOT ALLOW THE SAMPLE TO GO TO DRYNESS.

7.13 Final Extract Concentration - Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1-ml hexane to the top. Place the K-D apparatus on a hot water bath so that the concentrator tube is partially immersed 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 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.14 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of hexane. Reconnect the concentrator tube and concentrate the extract to a final volume of 1.0 ml. To ensure the final extract volume is accurate, the 10-ml K-D tube must be wiped dry. Weigh the 10-ml K-D tube with the extract and boiling chips to the nearest 0.1 gram. Transfer the extract to a 2-ml amber glass vial with Teflon-lined cap, and label as PCB fraction. Evaporate the small amount of hexane that may be left in the 10-ml K-D tube and reweigh. The final extract volume is calculated as shown below.

$$\textit{Volume (ml)} = [(\textit{initial weight (g)} - \textit{final weight (g)})] \times \frac{1}{0.660\ (\textit{density of hexane g/ml})}$$

The extract is ready for GC/ECD analysis. Store the extracts at 4°C (±2°C) in the dark until analyses are performed.

7.15 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in Calibration Standard #3 for GC/ECD analysis. Air or nitrogen blow-down is not allowed since its employment may result in intermittent loss of the more volatile PCB congeners.

8.0 Total Extractable Lipid Weight Determination

8.1 Record the weight of an aluminum weighing pan to $\pm$0.01 mg.

8.2 Transfer a known volume (approximately 5.0 ml) of the total sample extraction solution (see Section 7.6) to the aluminum weighing pan and record the weight to $\pm$0.01 mg.

8.3 Place the pan into a drying oven overnight at about 50° to 60° C, or on a hot plate (5 to 10 minutes), then into a dessicator to cool (10 to 15 minutes); and then weigh to $\pm$0.01 mg.

8.4 Return the sample to the oven (1 hour) or to the hot plate (5 minutes) and then a dessicator (10 minutes); and then reweigh.

8.5 Repeat step 8.4 until pan weights agree within $\pm$ 5%.

8.6 Record initial pan and all pan and lipid weights in a log book.

8.7 Measured lipid weight (mg) = (final wt of sample and pan [mg]) - (initial pan wt [mg])

8.8 Calculate total extractable lipid weight (TELW).

$$TELW = \frac{total\ sample\ volume\ (ml)}{lipid\ sample\ volume\ (ml)} \times measured\ lipid\ weight\ (mg)$$

Total sample volume and lipid sample volume are as measured in section 7.6.
Measured lipid weight as determined in step 8.7.

9.0 Quality Control

9.1 All reagents should be checked prior to use to verify that interferences (contamination) do not exist. New solvents and other reagents should be analyzed in a method blank prior to use on actual samples. These method blanks should be included in the GC run just prior to their intended use in the PCB congener extraction procedure.

9.2 Surrogate standards should be added to all samples, matrix spike samples, blanks, and standards.

9.3 A method blank should be extracted and cleaned-up with every extraction batch, each 20 samples, or Sample Delivery Group (SDG), which ever is more frequent. Method blanks are extracted with the samples to monitor for any interferences (contamination) introduced to the samples during preparation.

9.4 Matrix Spike and Matrix Spike Duplicate samples should be extracted for each 20 samples of a similar matrix collected over a 14-day period or each SDG, whichever is more frequent. The spiked compounds are used to monitor sample matrix effects which could interfere with the accuracy or precision of the PCB congener quantitations. If sample quantities are limited such that not enough material is available to perform matrix spike analyses, a certified tissue sample (reference sample) containing known amounts of polychlorinated biphenyls should be processed with each SDG to demonstrate method performance (e.g., NIST SRM 1589 standard material - PCBs [as Arochlor 1260] in human serum).

9.5 A Matrix Spike Blank should be extracted for each 20 samples of a similar matrix collected over a 14-day period or each SDG, whichever is more frequent. The spiked compounds are used to monitor the quantitative transfer of analytes through the extraction procedure, unaffected by any sample matrix interferences.

9.6 The spike standard should contain the most representative compounds at a concentration appropriate to the anticipated sample concentrations (see Table 1).

10.0 References

10.1 USEPA. 1990. "Test Methods for Evaluating Solid Waste" - Third Edition (SW-846) Revision 1. Method 3620A.

10.2 Bush, B., R.W. Streeter, and R.J. Sloan. 1989. Polychlorobiphenyls (PCB) Congeners in Striped Bass (Morone *saxilis*) from Marine and Estuarine Waters of New York State Determined by Capillary Gas Chromatography. Arch. Environ. Contam. Toxicol. 19:49-61.

10.3 W.D. MacLeod, et al. 1989. Analytical Procedures of the NOAA National Analytical Facility - Extractable Toxic Organic Compounds. National Maine Fisheries Service, Seattle, WA.

Table 1
PCB Congener Matrix Spiking Solution

Congener	Concentration (μg/ml)
2,4'-Dichlorobiphenyl	0.2
2,2',5-Trichlorobipheny	0.2
2,4,4'-Trichlorobiphenyl	0.2
2,2',3,5'-Tetrachlorobiphenyl	0.2
2,2',5,5'-Tetrachlorobiphenyl	0.2
2,3',4,4'-Tetrachlorobiphenyl	0.2
3,3',4,4'-Tetrachlorobiphenyl	0.2
2,2',4,5,5'-Pentachlorobiphenyl	0.2
2,3,3',4,4'-Pentachlorobiphenyl	0.2
2,3',4,4',5-Pentachlorobiphenyl	0.2
3,3',4,4',5-Pentachlorobiphenyl	0.2
2,2',3,3',4,4'-Hexachlorobiphenyl	0.2
2,2',3,4,4',5'-Hexachlorobiphenyl	0.2
2,2',4,4',5,5'-Hexachlorobiphenyl	0.2
2,2',3,3',4,4',5-Heptachlorobiphenyl	0.2
2,2',3,4,4',5,5'-Heptachlorobiphenyl	0.2
2,2',3,4',5,5',6-Heptachlorobiphenyl	0.2
2,2',3,3',4,4',5,6-Octachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	0.2

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3 Project Description

In accordance with the Scope of Work for the Hudson River PCB Reassessment RI/FS (December 1990) and the Final Phase 2 Work Plan and Sampling Plan (September 1992), Phase 2 of the Reassessment involves field sampling to further characterize and analyze site conditions at the Hudson River PCB Superfund Site. The Phase 2A Sampling and Analysis Plan/Quality Assurance Project Plan (Revision 2 dated May 29, 1992) described four sampling activities, including geophysical/confirmatory sediment sampling and high-resolution sediment coring (both of which have been completed) and water-column transect and water-column PCB equilibration studies (both of which are ongoing).

Phase 2B sampling will include five components, as described in the Final Phase 2 Work Plan and Sampling Plan: flow-averaged water-column sampling; benthic invertebrate and sediment sampling; low-resolution coring of Upper Hudson River sediments; analysis of archived water column and sediment samples on a PCB congener-specific basis; and sediment critical shear stress analysis. Only the benthic invertebrate and sediment (ecological) sampling is described in this report: **Volume 2 of the Phase 2B Sampling and Analysis Plan/Quality Assurance Project Plan (SAP/QAPjP).** Additional volumes of the Phase 2B SAP/QAPjP containing details of the remaining field programs will be submitted separately.

3.1 Background

3.1.1 Site Description

The Hudson River PCB Superfund site encompasses the Hudson River from Hudson Falls, N.Y. to the Battery in New York Harbor, a stretch of nearly 200 river miles. Because of their different physical and hydrologic regimes, the site has been designated by four (A, B, C and D) Study Areas (see Figures 3-1 and 3-2). The Final Phase 2 Work Plan and Sampling Plan, dated September 1992, provides more detail on each Study Area. This SAP/QAPjP covers ecological investigations in both the Upper Hudson (from Hudson Falls to Federal Dam; River Mile [R.M.] 197 to 153; Study Areas A and B) and in the Lower Hudson (from Federal Dam to the Battery; R.M. 153 to 0; Study Areas C and D).

3.1.2 *Site History*

During an approximately 30 year period ending in 1977, two General Electric (GE) facilities, one in Fort Edward and the other in Hudson Falls, NY, used PCBs in the manufacture of electrical capacitors. Various sources have estimated that between 209,000 and 1,300,000 pounds of PCBs were discharged between 1957 and 1975 from these two GE facilities. Discharges resulted from washing PCB-containing capacitors and minor spills.

The PCBs discharged to the river tended to adhere to sediments and accumulated downstream with the sediments as they settled in the impounded pool behind the former Fort Edward Dam. Because of its deteriorating condition, the dam was removed in 1973. During subsequent spring floods, PCB-contaminated sediments were scoured and released downstream. Exposed sediments from the former pool behind the dam, called the "remnant deposits," have been the subject of several remedial efforts.

Investigations at the site began after PCBs were reported in fish caught in the Upper and Lower Hudson in the early 1970's. In 1971, New York State Department of Environmental Conservation (NYSDEC) added PCBs to their statewide analyses of pesticide residues in fish, although no results were released publicly until 1975. After USEPA investigations in 1974 of PCB contamination in the Fort Edward area, NYSDEC intensified its PCB sampling program. In 1976, following the 1975-76 fish monitoring effort, NYSDEC banned all fishing in the Upper Hudson river from Albany north to Fort Edward due to the high levels of PCBs in fish. Commercial fishing for striped bass in the Lower Hudson was also banned at the same time. Both bans remain in effect. In addition to the ban on striped bass, New York has banned the sale of other Hudson River fish including American eel, white perch, carp, goldfish, brown bullhead, pumpkinseed sunfish, white catfish, and black crappie.

USEPA under the National Contingency Plan (NCP) and Comprehensive Environmental Responsive Compensation and Liability Act (CERCLA), or Superfund, performed a Feasibility Study (FS) in 1984 and issued a Record of Decision (ROD) for the site in 1984. The ROD called for: 1) an interim No Action alternative for river sediments; 2) in-place containment, capping, and monitoring of the remnant deposit sediments; and 3) a treatability study to evaluate the effectiveness of the Waterford Treatment Plant in removing PCBs from the river water. Since the signing of the ROD, planned remedial efforts of the remnant deposits has been completed,

B

APPENDIX B

CONVENTIONAL AND OTHER LAB ANALYSES

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Appendix B-3
Total Carbon/Total Nitrogen

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APPENDIX B-3

TOTAL CARBON AND TOTAL NITROGEN ANALYSIS OF RIVER SEDIMENT

1.0 Scope and Application

1.1 This procedure determines the total carbon content and total nitrogen content of a small (<0.5 g) sediment sample. The procedure is based on Verardo, et. al., 1990. The procedure measures the combined masses of the inorganic and organic forms of carbon and nitrogen.

2.0 Summary of Method

2.1 A measured mass of dried sediment, approximately 5 to 10 mg, is combusted at 1050°C. The resulting gases pass over a solid catalyst (chromium trioxide (Cr_2O_3) on a silvered cobalt oxide base (Co_3O_4+Ag)). The resulting gases pass over a second catalyst (metallic copper) to convert nitrogen oxides to N_2. The exhaust stream then passes through a column containing magnesium perchlorate to remove water vapor. The cleaned gas stream is then analyzed by gas chromatography for CO_2 and N_2 using a thermal conductivity detector.

2.2 The instrument used is a modified Carlo Erba NA-1500 Analyzer.

2.3 No method interferences are known.

3.0 Apparatus and Materials

3.1 Carlo Erba NA-1500 Analyzer - modified for this method.

3.2 50-unit sample delivery carousel

3.3 Catalytic column containing a porous layer of chromium trioxide (Cr_2O_3) overlaying silvered cobalt oxide.

3.4 Catalytic column containing metallic copper.

3.5 Absorption column containing magnesium perchlorate.

3.6 Tin sample cups.

4.0 Reagents

4.1 Calibration Standard: $CH_3CON(CH_3)C_6H_4OH$, a derivative of acetanilide, an NBS standard (#141C) with a C/N weight ratio of 6.86 and a C/N molar ratio of 8. This standard is weighed out into 3 or 4 standard weight aliquots to completely encompass the anticipated range of sample C and N levels.

5.0 Initial Calibration

5.1 The measurement system is calibrated once per 50-sample carousel run. Each calibration consists of five measured amounts of the acetanilide standard containing approximately 100, 300, 600, 800, and 1000 ug of carbon and a standard blank (empty sample cup); standard ranges will bracket sample concentrations. Since the instrument measures total carbon and total nitrogen mass generated, the standardization consists of measurements of known amounts of carbon and nitrogen.

5.2 The initial calibration is followed by a method blank (MB), consisting of an empty sample cup.

5.3 The method blank is followed by analysis of an ICV which will be from a separate source than the calibration standards.

5.4 The continuing calibration verification (CCV) will be a mid-range acetanilide standard analyzed at the minimum frequency of every 20 samples.

6.0 Sample Preparation

6.1 All sediment samples will be dried in an incubator under a controlled atmosphere. (A controlled atmosphere is maintained in the incubator by using a purging system which consists of a clean air source and a florisil column for removing PCBs and other organic contaminants from air.) After drying, the sediments are ground with a mortar and pestle to remove lumps and minimize sample heterogeneity. The anticipated analytical sample size (aliquot) is 5 to 10 mg, although this size may be adjusted as necessary to meet detection limit and precision goals.

7.0 Calculations

7.1 The results of the initial calibration, including the 4 standards and blank, are used to prepare a calibration curve. A first or second order regression equation may be used to fit the data. No higher order of regression is allowed. The correlation coefficient for the calibration must be ≥ 0.995. A plot of the calibration curve must be supplied with the sample results.

7.2 Repeat procedure 7.1 for the nitrogen results.

7.3 Calculate the mass of carbon and the mass of nitrogen for each of the samples, laboratory control checks and blanks using the established initial calibration curve for that run.

7.4 Calculate the concentration of carbon in a sample as follows:

$$\textit{Carbon Concentration (\%)} = \frac{\textit{mass of carbon generated (ug)}}{\textit{mass of sample (mg)}} \times \frac{1\ mg}{1000\ ug} \times 100\%$$

7.5 Similarly calculate the concentration of nitrogen in a sample:

$$\textit{Nitrogen Concentration (\%)} = \frac{\textit{mass of nitrogen generated (ug)}}{\textit{mass of sample (mg)}} \times \frac{1\ mg}{1000\ ug} \times 100\%$$

7.6 Calculate carbon to nitrogen weight ratio for each sample, internal standard and blank as follows:

$$C/N\ (wt) = \frac{\textit{Carbon Concentration (\%)}}{\textit{Nitrogen Concentration (\%)}}$$

7.7 Calculate the carbon to nitrogen moles ratio for each sample, internal standard and blank as follows:

$$C/N\ (Mole) = \frac{\left(\frac{\textit{Carbon Concentration (\%)}}{12}\right)}{\left(\frac{\textit{Nitrogen Concentration (\%)}}{14}\right)}$$

7.8 Calculate the relative percent difference (RPD) for all duplicate pairs for the nitrogen concentration, carbon concentration, and the C/N ratio as follows:

$$RPD = \frac{Sample\ Level - Sample\ Duplicate\ Level}{\left(\frac{Sample\ Level + Sample\ Duplicate\ Level}{2}\right)} \times 100\%$$

8.0 Precision and Accuracy

8.1. The precision of the carbon and nitrogen determination is largely dependent on the precision of the sample weighing. The criterion for precision is $\leq 10\%$ on laboratory duplicate pairs.

8.2 The minimum detection limits for carbon and nitrogen are 0.01% and 0.001% by weight respectively.

8.3 The criterion for accuracy of the LCS measurement is 90-100% recovery for the NBS standard.

9.0 Quality Control

9.1 Method Blank

9.1.1 A method blank, consisting of an empty sample cup, will be analyzed at the frequency of one for every 20 samples or sample delivery group (SDG), whichever is more frequent. Three blanks are included for each 50 slot carousel run.

9.1.2 Method blanks must not exceed the minimum detection limits for carbon and nitrogen and will be reported in the final data report.

9.1.3 If a laboratory method blank exceeds these criteria, the laboratory must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) must be reanalyzed. The Laboratory Manager, or his designee, must address problems and solutions in the Case Narrative, which will accompany the data report.

9.1.4 The laboratory must report all sample concentration data as uncorrected for blank contamination.

9.2 Laboratory Standards

9.2.1 All internal laboratory standards (LCS) must recover within 90-110% for carbon concentration, nitrogen concentration or the C/N ratios. If any laboratory standard exceeds criteria, all samples analyzed since the last time the criteria was met must be reanalyzed.

10.0 References

10.1 Verardo, D.J., P.N. Froelich, and A. McIntyre. Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer, *Deep Sea Research* 37, 157-165 (Instruments and Methods Section), 1990.

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Appendix B-4
Total Inorganic Carbon

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APPENDIX B-4

TOTAL INORGANIC CARBON ANALYSIS OF RIVER SEDIMENT

1.0 Scope and Application

This procedure determines the total inorganic carbon content of a small (< 100 mg) sediment sample. The procedure is applicable to sediments containing 0.01% to 10% carbon in an inorganic form.

2.0 Summary of Method

An aliquot of dried sediment of about 50 mg is placed in a reaction vessel. The sample is then treated with an excess of concentrated acid and the resulting CO_2 is swept from the reaction chamber to a coulometer which determines the moles of CO_2 generated. From these results the amount of inorganic carbon in total μg can be calculated.

3.0 Apparatus and Materials

3.1 CO_2 - coulometer made by Coulometrics, Inc. with associated reaction chamber and electrolytic cell.

3.2 Electrolyte solution from Coulometrics, Inc. containing monoethanolamine.

3.3 Precision balance - with an accuracy of $\pm$0.05 mg.

3.4 Glass reaction vessels.

4.0 Reagents

4.1 Concentrated hydrochloric (HCl) or sulfuric acid (H_2SO_4).

4.2 Carrier Gas - Nitrogen or air, CO_2-free.

4.3 Calibration Standard - Pure $CaCO_3$ (calcium carbonate).

5.0 Initial Calibration

5.1 The initial calibration will consist of a one point calibration derived from a standard weight of calcium carbonate plus a standard blank (empty reaction vessel).

5.2 After standardizing the instrument, analyze an initial calibration verification (ICV) standard. This ICV must be from a separate source than the calibration standard and must recover within 90% to 110% of the true value (source: Oregon State University).

6.0 Procedure

6.1 Place the weighed aliquot of sediment sample ($\leq$ 50 mg) in reaction vessel.

6.2 Purge reaction vessel with CO_2 - free carrier gas for approximately 2 minutes.

6.3 Add sufficient concentrated acid for complete conversation of inorganic carbon to CO_2.

6.4 Record total μg of carbon as measured by the instrument.

7.0 Calculations

7.1 Calculate the sample value for total inorganic carbon using the initial calibration curve generated with the samples.

7.2 Calculate the relative percent difference (RPD) for duplicate pairs as follows:

$$RPD = \frac{Sample\ Level - Sample\ Duplicate\ Level}{\left(\frac{Sample\ Level + Sample\ Duplicate\ Level}{2}\right)} \times 100\%$$

7.3 Calculate % recovery of the initial calibration verification (ICV) and the continuing calibration verification (CCV) as follows:

$$\%\ Recovery = \frac{Observed\ Value}{True\ Standard\ Value} \times 100\%$$

8.0 Precision and Accuracy

8.1 The criterion for duplicate precision of the method is ≤10% RPD.

8.2 The minimum detection limit is anticipated to be 0.02% total inorganic carbon (200 mg/kg) on a 50 mg sample.

8.3 The criteria for accuracy of the ICV and CCVs are 90% to 110% recoveries.

9.0 Quality Control

9.1 Method Blank

9.1.1 Method blanks are generated using an empty reaction vessel. The method blank is then analyzed via the procedure given in Section 6.

9.1.2 The method blank should not exceed the detection limit given in Section 8. If this occurs, all samples analyzed since the last acceptable blank level was obtained must be reanalyzed.

9.1.3 Method blanks are analyzed for every 20 samples or each sample delivery group which ever is more frequent.

9.2 Initial Calibration

The calibration must be performed daily. If the ICV does not meet criteria, the instrument must be recalibrated and the ICV reanalyzed until criteria is met.

9.3 Continuing Calibration Verification (CCV)

A mid-range standard, CCV, will be analyzed after every 10 samples and at the end of the day's operation to check instrument drift. This standard must agree to within 10% of the true value. If this is not achieved, all samples analyzed since the last time the CCV was in control must be rerun. The laboratory must first re-establish control by recalibrating the instrument and rerunning the ICV as an initial check prior to continuing sample analyses.

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Appendix B-5
Grain-Size Distribution (laser)

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APPENDIX B-5

GRAIN-SIZE DISTRIBUTION (LASER)

Samples are well-mixed prior to analysis in order to obtain a representative subsample. The methodology will combine measurements made by standard sieving techniques for the gravel fraction where necessary and the measurements obtained on a Malvern 2600L laser particle sizer (see manufacturer's instructions for QC and operation).

The Malvern instrument is calibrated at the factory. It employs lenses of different focal lengths to measure the concentration of particles within a maximum size range of 1800 um to 1 um. Sub-samples are introduced into the Malvern by first disaggregating in a water bath by mechanical stirring and ultrasonic dispersion. It may be required with certain samples to perform two laser measurements: one to encompass the sand fraction; and the other for the silts. In this case, the separate distributions and the sieve data are "merged" together using an algorithm to reproportion the weight percents into a single, complete distribution.

The merging algorithm must be mathematically correct; there must be appropriate overlap in the tails of the different distributions in order for the merging to be consistent. This approach, or an equivalent, should be employed to give the required complete distribution from gravel (4mm) to clay (0.001 mm) particles. For the smaller size particles, 0.120 mm to 0.001 mm, 16 sizes fractions must be defined.

Analysis: Particle size distribution for 500 g and 5 g sample sizes must encompass range of 4 mm down to 0.001 mm (1 um).

METHOD	QC REQUIREMENTS
Laser Size Methodology (recommended Malvern 2600L) or equivalent for particle sizes down to 0.001 mm (1 um) and small sample aliquots.	- Duplicate performed at 5% frequency - Duplicate % Similarity: $\geq$ 80% - Field duplicates as delivered (estimate 5% frequency)

% Similarity = the sum of the lower of the two percentages for each band size in a sample pair.

For example:

Size Band	A	B	C	D		
% Sample	7	3	40	50	=	100%
% Duplicate	4	5	42	49	=	100%
Smallest %	4	3	40	49	=	96% Similarity

Appendix B-7
Organic Carbon in Sediment (L. Kahn Method)

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DETERMINATION OF TOTAL ORGANIC CARBON IN SEDIMENT

1. Scope and Application

1.1 This method describes protocols for the determination of organic carbon in ocean sediments.

1.2 Although the detection limit may vary with procedure or instrument, a minimum reporting value of 100 mg/kg will be required for the ocean dumping/dredging program.

1.3 Several types of determinations, which are considered equivalent are presented.

1.4 Data are reported in mg/kg on a dry weight basis.

1.5 Wet combustion methods are not considered to be equivalent to the pyrolytic methods herein described.

2. Summary of Method

2.1 Inorganic carbon from carbonates and bicarbonates is removed by acid treatment.

2.2 The organic compounds are decomposed by pyrolysis in the presence of oxygen or air.

2.3 The carbon dioxide that is formed is determined by direct non-dispersive infrared detection, flame ionization gas chromatography after catalytic conversion of the carbon dioxide to methane; thermal conductivity gas chromatography, differential thermal conductivity detection by sequential removal of water and carbon dioxide; or thermal conductivity detection following removal of water with magnesium perchlorate.

2.4 Water content is determined on a separate portion of sediment.

3. Sample Handling and Preservation

3.1 Collect sediments in glass jars with Teflon or aluminum foil. Cool and maintain at 4°C. Analyse within 14 days.

4. Interferences

4.1 Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias.

4.2 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4°C, analyzing within the specified holding time, and analyzing the wet sample.

3. Apparatus

5.1 Drying oven maintained at 103° to 105°C.

5.2 Analytical instrument options:

5.2.1 Perkin Elmer Model 240C Elemental Analyser or equivalent.

5.2.1.1 In this instrument, the sample from Section 7.2 is pyrolyzed under pure oxygen, water is removed by magnesium perchlorate and the carbon dioxide is removed by ascarite. The decrease in signal obtained by differential thermal conductivity detectors placed between the combustion gas stream before and after the ascarite tube is a measure of the organic carbon content.

5.2.2 Carlo Erba Model 1106 CHN Analyser, or equivalent.

5.2.2.1 In this apparatus, the sample is pyrolyzed in a induction type furnace, and the resultant carbon dioxide is chromatographically separated and analyzed by a differential thermal conductivity detector.

5.2.3 LECO Models WR12, WR112, or CR-12 carbon determinators, or Models 600 or 800 CHN analysers.

5.2.3.1 In the LECO WR-12, the sample is burned in high frequency induction furnace, the carbon dioxide is selectively adsorbed at room temperature in a molecular sieve. It is subsequently released by heating and is measured by a thermal conductivity detector. The WR-112 is an upgraded WR-12 employing microprocessor electronics and a printer to replace the electronic digital voltmeter.

5.2.3.2 In the LECO CR-12 carbon determinator, the sample is combusted in oxygen, moisture and dust are removed by appropriate traps and the carbon dioxide is measured by a selective, solid state, infrared detector. The signal from the detector is then processed by a microprocessor and the carbon content is displayed on a digital readout and recorded on an integral printer.

5.2.3.3 In the LECO CHN-600 and CHN-800 elemental analysers, the sample is burned under oxygen in a resistance furnace and the carbon dioxide is measured by a selective infrared detector.

5.2.4 Dohrman Model DC85 Digital High Temperature TOC Analyser.

5.2.4.1 In this instrument, the sample is burned in resistance furnace under oxygen, the interfering gases are removed by a sparger/scrubber system and the carbon dioxide is measured by a non-dispersive infrared detector and shown on a digital display in concentration units.

5.3 No specific analyzer is recommended as superior. The above listing is for information only and is not intended to restrict the use of other unlisted instruments capable of analysing TOC. The instruments to be used must have the following specifications:

5.3.1 A combustion boat which is heated in a stream of oxygen or air in a resistance or induction-type furnace to completely convert organic substances to CO_2 and water.

5.3.2 A means to physically or by measurement technique to separate water and other interferants from CO_2.

5.3.3 A means to quantitatively determine CO_2 with adequate sensitivity (100 ng/kg), and precision (25% at the 95% confidence level as demonstrated by repetitive measurements of a well mixed ocean sediment sample).

5.4 A strip chart or other permanent recording device to document the analysis.

6. Reagents

6.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank.

6.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

6.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

6.4 Phosphoric acid solution, 1:1 by volume.

7. Procedure

7.1 Weigh the well mixed sample (up to 500 mg) into the combustion boat or cup. Add 1:1 phosphoric acid drop wise until effervescence stops. Heat to 75°C.

NOTE: This procedure will convert inorganic carbonates and bicarbonates to carbon dioxide and eliminate it from the sample.

7.2 Analyze the residue according to the instrument manufacturer's instructions.

7.3 Determine percent residue on a separate sample aliquot as follows:

7.3.1 Heat a clean 25 ml beaker at 103° to 105°C for one hour. Cool in desiccator, weigh to the nearest mg and store in desiccator until use.

7.3.2 Add 1 g, weighed to the nearest mg, of an aliquot of the well-mixed sample.

7.3.3 Dry and heat in the 103° to 105°C oven for one hour. Cool in desiccator. Weigh to the nearest mg.

8. Calibration

8.1 Follow instrument manufacturer's instructions.

8.2 Prepare calibration curve plotting mg carbon vs. instrument response, using four standards and a blank covering the analytical range of interest.

9. Precision and Accuracy

9.1 The precision and accuracy will differ with the various instrume and matrices and must be determined by the laboratories reportin data. To initiate a control chart, a representative sample of well mixed sediment should be analyzed 15 times to determine the analytical precision. Set up a control chart showing 3 times the standard deviation limits for precision.

9.2 Subsequently during analysis of environmental samples, take one sample per batch of 20 or less and run in quadruplicate. Calculate standard deviation and report with initial control chart data.

9.3 If the sample being run in quadruplicate exceeds the 3 standard deviation limit, identify error and rerun environmental samples in that batch along with the quadruplicate sample.

Appendix B-8
Species Diversity/Abundance and Biomass Determination for Benthic Invertebrates

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APPENDIX B-8

SPECIES DIVERSITY/ABUNDANCE AND BIOMASS DETERMINATION FOR BENTHIC INVERTEBRATES

1. SUMMARY OF METHOD

1.1 The sample is washed and sieved to remove sediment and debris, and large organic matter is removed.

1.2 The total biomass is determined by weighing the remaining material.

1.3 The total biomass is then sorted to the lowest possible taxonomic group (species) under a low power screening lens or magnifying lamp.

2. APPARATUS AND MATERIALS

2.1 Clean water, for rinsing samples.

2.2 U.S. Standard No. 30 mesh sieve (0.5 mm opening).

2.3 Analytical balance, capable of weighing to $\pm$0.1 mg.

2.4 Low power scanning lens or magnifying glass.

2.5 Compound microscope for examination of chironomids and oligochaetes.

2.6 Whatman #40 filter paper or equivalent.

2.7 Spatula and forceps.

2.8 White enameled pan (approx 6" by 9").

2.9 Filtration apparatus.

3. PROCEDURE

3.1 Prepare the sample by washing through a U.S. Standard No. 30 mesh (0.5 mm openings) sieve to remove any fine sediment. Any large organic material (whole leaves, twigs, algal or macrophyte mats) should be rinsed, visually inspected, and discarded.

3.2 The sample is then placed in a white enamel pan, filled approximately one-third with water, and distributed evenly over the bottom of the pan. It is then sorted using a low-power scanning lens or magnifying lamp. The sample should be sorted and examined repeatedly to remove all organisms

3.2.1 For samples that are judged to contain more than 1,000 individuals, one-half or one-quarter subsamples may be examined. The subsampling is done by placing the sample in a tray, evenly distributing it over the bottom, and placing a divider in the tray which divides the sample into quarters. For samples with a large number of a particular group of organisms, the numerous group of organisms may be subsampled, while the remaining organisms are sorted from the entire sample. Sorted specimens of all samples are archived for possible future analysis.

3.2.2 Organisms should be identified to the species level when possible. The level of identification for major groups specified by NYSDEC (1991) will be used. Chironomidae are subsampled for 100 individuals, and Oligochaeta are subsampled for 50 individuals. The number of individuals in each species is recorded on a Laboratory Data Sheet (Figure 1). Representative specimens from a sample are selected and stored separately in a reference collection. The reference collection of identified specimens is maintained for comparative and quality control purposes.

3.3 Transfer the organisms to a piece of filter paper (Whatman #40 or equivalent) and filter the sample by vacuum to remove as much of the water as possible. Determine the biomass (wet weight) of the major taxa and the total sample biomass.

3.4 After sorting is completed, the organisms will be dried in an oven at 100° C and weighted to $\pm$0.1 mg to determine the dry weight of the major taxa and the total sample biomass.

4. REFERENCES

NYSDEC, 1991. Methods for Rapid Biological Assessment of Streams. Stream Biomonitoring Unit, Division of Water.

FIGURE 1

LABORATORY DATA SHEET

LABORATORY DATA SHEET

New York State Department of Environmental Conservation

Individuals
Taxa
Subsample: entire 1/2 1/4 100
Sorted by:
est. biomass

River/stream
Station number
Date
Sample type

	subsample	total
PLATYHELMINTHES		
OLIGOCHAETA		
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
HIRUDINEA		
MOLLUSCA		
1.		
2.		
3.		
4.		
5.		
CRUSTACEA		
ACARIFORMES		
MEGALOPTERA		
EPHEMEROPTERA		
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10		
11.		
12.		
PLECOPTERA		
OTHER INSECTA		

	subsample	total
COLEOPTERA		
1.		
2.		
3.		
4.		
5.		
TRICHOPTERA		
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
OTHER DIPTERA		
1.		
2.		
3.		
4.		
5.		
CHIRONOMIDAE larvae		
pupae		
total		
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
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C

APPENDIX C

FIELD PROCEDURES

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C-1
Sample Packaging and Shipping SOP

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1. OBJECTIVE

This guideline provides instructions for sample packaging and shipping of Contract Lab Program (CLP) samples in accordance with USEPA guidelines and U.S. Department of Transportation (USDOT) regulations.

2. APPLICABILITY

The guideline is applicable to shipment of all samples taken from controlled or uncontrolled hazardous substance sites for analysis at laboratories away from the site.

3. LIMITATIONS

These guidelines are to be used for low and medium concentration samples collected from hazardous substance sites. High concentration hazardous substance samples and radiation samples are not covered by this SOP.

4. DEFINITIONS

"Carrier" -- A person or firm engaged in the transportation of passengers or property.

"N.O.S." -- Not otherwise specified.

"N.O.I." -- Not otherwise indicated.

"ORM" -- Other regulated material.

"Environmental Samples" -- Samples with medium or low contaminant concentrations such as ambient air, streams, groundwater, leachates, ditches, soil, and sediments collected at a distance from direct sources of contaminants.

"USDOT Classifications for Hazardous Materials" -- Classifications used to classify materials for shipment are set forth by the USDOT in the Code of Federal Regulations (49 CFR 173.2):

5. GUIDELINES

Samples collected at controlled or uncontrolled hazardous substance sites usually are transported elsewhere for analysis. Samples shall be transported so as to protect their integrity, as well as to protect against any detrimental effects from

leakage or breakage. Regulations for packaging, marking, labeling, and shipping hazardous materials and wastes are promulgated by the U.S. Department of Transportation and described in the Code of Federal Regulations (49 CFR 171 through 177, in particular 172.402h, Packages Containing Samples collected at controlled or uncontrolled hazardous waste sites or samples collected during emergency responses). However, the USEPA has agreed through a memorandum of agreement to package, mark, label, and ship samples observing USDOT procedures.

5.1 RESPONSIBILITIES

The field SMO and ultimately the team leader is responsible for determining that the hazardous substance site samples are properly packaged and shipped. Sampling personnel are responsible for implementing the packaging and shipping requirements. The Chain-of-Custody procedures and requirements are described in TAMS' Standard Operating Procedure No. 60.

5.2 EQUIPMENT

The following equipment is used in packaging and shipping low concentration samples:

1. Sample bottles (provided by TAMS).
2. Polyethylene bags (2 mil or thicker).
3. Packing materials such as vermiculite, or "slick wick".
4. Picnic coolers or ice chests (preferably constructed of metal) capable of withstanding impact caused by a 4-foot drop.

The following additional equipment is used in packaging and shipping medium concentration samples:

1. Metal paint cans and lids (1 gallon or other sizes as appropriate).

5.3 ENVIRONMENTAL SAMPLES

5.3.1 Low Concentration Environmental Samples

5.3.1.1 Packing

Each environmental sample is packaged in a separate sealable polyethylene bag (both VOA vials may be put in one bag) and packed in metal (picnic cooler-type) containers. Sufficient noncombustible, absorbent cushioning material such as vermiculite will be used to minimize the possibility of sample container breakage. Ice is added to the cooler when sample preservation is required.

Ice cubes are put in sealable polyethylene bags and placed around samples before the packing material covers the bottles.

Organic and inorganic fractions are sent to separate laboratories. These fractions may be further split by matrix such that organic water samples may go to one lab and organic soil samples to another. SAS samples will also be shipped to a separate laboratory. If only soil samples are collected, field blanks and trip blanks will be sent, with the soil samples, to their respective organic and inorganic labs.

5.3.1.2 Marking and Labeling

A complete sample identification tag (as explained in SOP No. 60) shall be affixed to sample containers.

An address label shall be affixed to the shipping container, along with proper labels (e.g., "This End Up").

No USDOT marking or labeling is required.

5.3.1.3 Shipping Papers

No USDOT shipping papers are required for environmental samples. However, the appropriate Chain-of-Custody forms shall be included with the shipment.

5.3.1.4 Transportation

There are no USDOT restrictions on the mode of transportation for low concentration environmental samples.

5.3.2 Medium Concentration Environmental Samples

The procedures to be used to pack, label, mark, and ship hazardous waste samples are presented below.

5.3.2.1 Packaging

Packaging procedures are as follows:

a. After collection of sample in a properly labeled bottle (see TAMS SOP No. 60), seal sample bottle with a custody seal and place in 2 mil thick (or thicker) sealable polyethylene bag (one sample bottle per bag except VOA vials). Tags shall be positioned to enable visibility through the bag.

b. Place sealed bag inside a metal can with incombustible, absorbent cushioning (e.g., vermiculite) to deter breakage (one bag per can). Pressure-close the can and use clips, tape or other means to secure the lid tightly and effectively. Two VOA vials may be placed in one metal can.

c. Mark and label this container with CLP sample number and date.

d. Place one or more metal cans, surrounded by incombustible packaging material for stability during transport, into a metal picnic cooler. Place the ice (in sealed polyethylene bags) adjacent to the metal cans.

e. Mark and label the shipping container and complete shipping documents as described below.

5.3.2.2 Marking and Labeling

Use abbreviations only where specified. Place the following information (either hand-printed or on preprinted labels) on the cooler: laboratory name and address and "Flammable Liquid, N.O.S." (if not liquid, write "Flammable Solid, N.O.S."). Place the following labels on the outside of the cooler: "Cargo Aircraft Only" and "Flammable Liquid" (if not liquid, "Flammable Solid"). ("Dangerous When Wet" label should be used if the solid has not been exposed to wet environment.) Using "Flammable" does not convey the certain knowledge that a sample is in fact flammable, or how flammable, but is intended to prescribe the class of packaging in order to comply with DOT regulations.

The cooler shall also have "Laboratory Samples" and "THIS SIDE UP" (or "THIS END UP") marked on the top of the shipping cooler, and upward-pointing arrows should be placed on all four sides of the shipping cooler.

5.3.2.3 Shipping Papers

Complete the shipper's certification section of the airbill (Fig. 61.1) in the following manner:

1. Check "49 CFR"
2. Fill in number of coolers to be shipped
3. Fill in proper shipping category
   - "Flammable Solids N.O.S." or "Flammable liquids N.O.S."
   - Limited quantity; cargo aircraft only

"Limited quantity" indicates:

Solids: the fraction of solids inside the glass container shall not exceed one pound net weight and the net quantity of solids in each cooler shall not exceed 25 lbs.

Liquids: liquids in volume of 32-oz or less are placed in metal cans and then packed in a durable outside (exterior) container. These are shipped cargo aircraft only, as the total volume in the cooler exceeds the one quart limit set for passenger aircraft (49 CFR173.118). Coolers shall not exceed 10 gallons flammable liquid N.O.S. when shipped by cargo aircraft.

4. Class or Division
   Fill in "Flammable Liquid or Flammable Solid" N.O.S.

5. UN or ID Number
   Flammable Liquid UN 1993 or Flammable Solid UN 1325

6. Subsidiary Risk
   (Leave Blank)

7. Total Net Quantity

   For Solids: State the number of coolers and the net quantity of flammable solid N.O.S. contained in each cooler (e.g., 2 @ 5 lbs.).

   For Liquids: State the number of coolers and then state the net quantity of flammable liquids in each cooler (e.g., 1@ 2 gallons).

   The net volume for each cooler cannot exceed 10 gallons of flammable liquid N.O.S.

8. Packing Instructions
(Leave Blank)

9. Authorization
(Leave Blank)

10. Additional Description Requirements for Radioactive Materials
(Leave Blank)

11. Shipping Limitations
Circle: "Cargo Aircraft Only"

12. Airport Departure/Destination
(Leave Blank: Federal Express agent will fill in

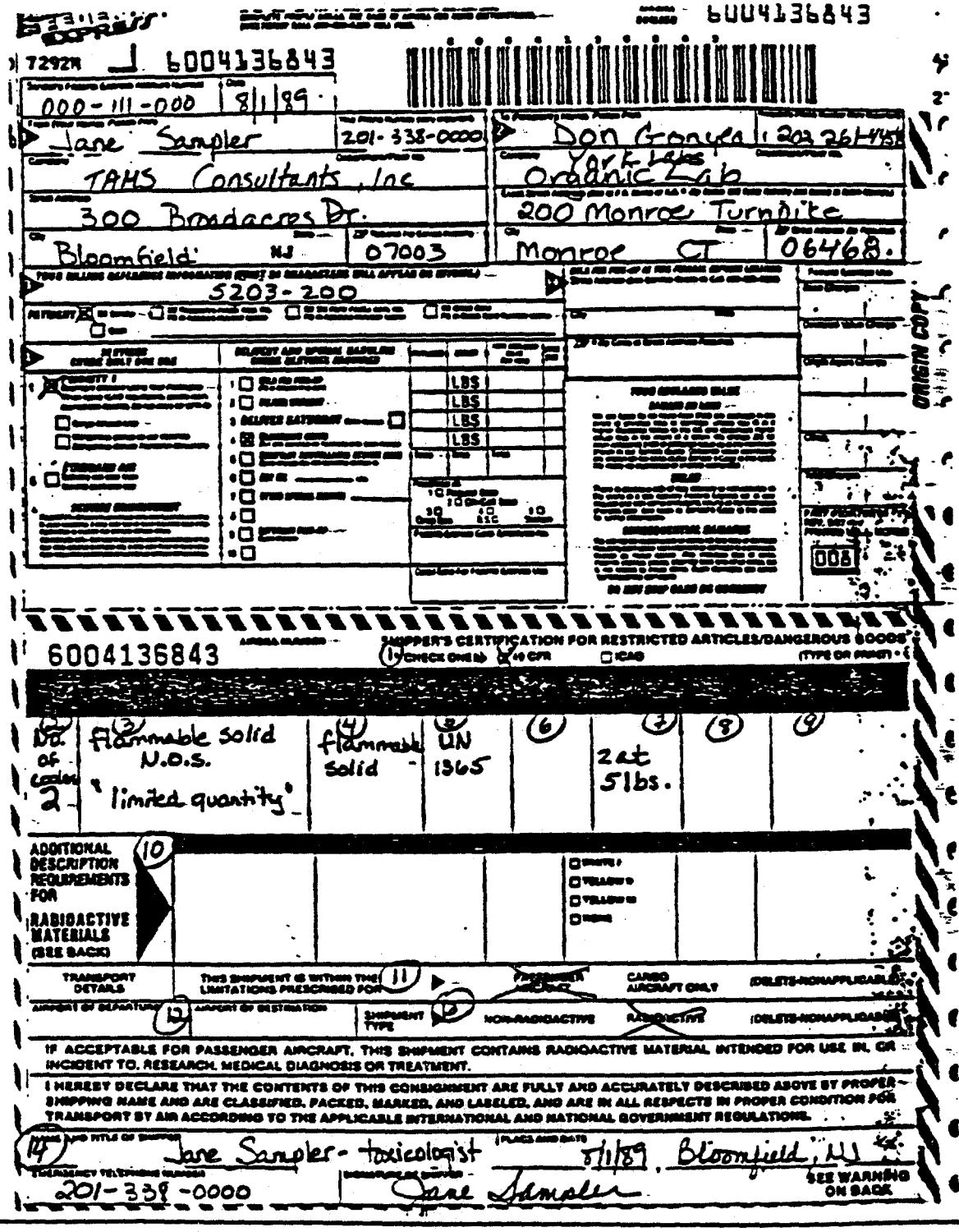
13. Shipment Type
Circle: "Non-radioactive"

14. Print Name & Title
TAMS Telephone Number
Signature of Shipper

Refer to Figure 61-1 for completed airbill/shipper's certification form. A Chain-of-Custody form (see Standard Operating Procedure No. 60) shall be executed and placed in the exterior container.

FIGURE 61-1 - AIRBILL/SHIPPER'S CERTIFICATION FORM

FIGURE 61-1 - AIRBILL/SHIPPER'S CERTIFICATION FORM



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72928 6004136843

000-111-000 | 8/1/89

Jane Sampler | 201-338-0000

TAHS Consultants, Inc

300 Broadacres Dr.

Bloomfield NJ 07003

Don Gonyea | 203 261-4451

York Labs

Organic Lab

200 Monroe Turnpike

Monroe CT 06468

5203-200

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LBS

LBS

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LBS

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SHIPPER'S CERTIFICATION FOR RESTRICTED ARTICLES/DANGEROUS GOODS

(1) CHECK ONE ☒ 49 CFR ☐ ICAO (TYPE OR PRINT)

(2a) No. of coolers	(3)	(4)	(5)	(6)	(7)	(8)	(9)
2	Flammable solid N.O.S. 'limited quantity'	flammable solid	UN 1365		2 at 5lbs.		

(10) ADDITIONAL DESCRIPTION REQUIREMENTS FOR RADIOACTIVE MATERIALS (SEE BACK)

TRANSPORT DETAILS | (11) THIS SHIPMENT IS WITHIN THE LIMITATIONS PRESCRIBED FOR: PASSENGER AIRCRAFT | CARGO AIRCRAFT ONLY | (DELETE-NONAPPLICABLE)

(12) AIRPORT OF DEPARTURE | AIRPORT OF DESTINATION | (13) SHIPMENT TYPE | NON-RADIOACTIVE | RADIOACTIVE | (DELETE-NONAPPLICABLE)

IF ACCEPTABLE FOR PASSENGER AIRCRAFT, THIS SHIPMENT CONTAINS RADIOACTIVE MATERIAL INTENDED FOR USE IN, OR INCIDENT TO, RESEARCH, MEDICAL DIAGNOSIS OR TREATMENT.

I HEREBY DECLARE THAT THE CONTENTS OF THIS CONSIGNMENT ARE FULLY AND ACCURATELY DESCRIBED ABOVE BY PROPER SHIPPING NAME AND ARE CLASSIFIED, PACKED, MARKED, AND LABELED, AND ARE IN ALL RESPECTS IN PROPER CONDITION FOR TRANSPORT BY AIR ACCORDING TO THE APPLICABLE INTERNATIONAL AND NATIONAL GOVERNMENT REGULATIONS.

(14) NAME AND TITLE OF SHIPPER: Jane Sampler - toxicologist | (PLACE AND DATE) 8/1/89, Bloomfield, NJ

EMERGENCY TELEPHONE NUMBER: 201-338-0000 | SIGNATURE OF SHIPPER: Jane Sampler

SEE WARNING ON BACK

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C-2
pH - Field Measurement SOP for Waters

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C-2
pH - Field Measurement SOP for Waters

1. OBJECTIVE

This guideline details the steps required to measure the pH of an aqueous sample while in the field using either a pH meter or pH paper. It is important to obtain a pH measurement soon after taking a sample and thus avoid sample changes such as precipitation, temperature fluctuation, or oxidation, which can affect the pH of the sample.

2. LIMITATIONS

This guideline is applicable to aqueous samples such as potable well water, monitoring well water, surface water, leachate, and drummed wastewater.

3. DEFINITIONS

"pH" -- The negative logarithm (base 10) of the hydrogen ion activity. The hydrogen ion activity is related to the hydrogen ion concentration, and, in relatively weak solution, the two are nearly equal. Thus, for all practical purposes, pH is a measure of the hydrogen ion concentration.

"pH Paper" -- Paper that turns different colors depending on the pH of the solution to which it is exposed. Comparison with color standards supplied by the manufacturer will then give an indication of the solution pH.

4. GUIDELINES

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment such as acid-base neutralization, water softening, and corrosion control is pH dependent.

Two methods are given for pH measurement: the pH meter, and pH indicator paper. The indicator paper is used when only a rough estimate of the pH is required. For this program pH paper will be used to verify sample preservation when pH <2 must be maintained. The pH meter is used when a more accurate measurement is needed, usually within 0.01 to 0.1 pH units. All pH water analyses will employ the pH meter method. To use the pH meter, the meter with electrode are standardized using pH 7, pH 4, and pH 10 buffers. The probe is then immersed in the unknown sample aliquot to obtain a pH reading. No standardization is required when using pH paper. A small aliquot of acidified sample will be used to moisten the pH paper for verification of acidification.

4.1 RESPONSIBILITIES

The project team leader is responsible for deciding when a pH measurement should be taken.

The field samplers are responsible for measuring the pH and for recording and reporting the results.

4.2 EQUIPMENT

The following equipment is needed for taking field pH measurements:

4.2.1 pH Measurements by paper

pH indicator paper, such as Hydrion or Alkacid, to cover the pH range 1 through 12. pH paper is available in a variety of ranges, depending on the accuracy required. pH paper is typically used when checking the proper preservation of aqueous samples.

4.2.2 pH Measurements by instruments:

1. Portable pH meter or equivalent; model #HI 9025, Hanna; Model #103, Corning.

2. Combination electrode with polymer body to fit the meter.

3. pH buffer (standard) solutions (recommended standards are 4.0, 7.0, and 10.0)

4. Clean glass or plastic containers (e.g., disposable 50 ml beakers)

4.3 FIELD pH MEASUREMENT

4.3.1 pH Meter

The following procedure is used for measuring pH with a pH meter:

1. Immerse the tip of the electrode in pH 7 buffer vernight. If this is not possible due to field conditions, immerse the electrode tip in pH 7 buffer for at least an hour before use. (Probes should be stored with the plastic liquid cup attached so as to minimize the stabilization period required and to prevent the wick from drying out.)

2. Rinse the electrode with demineralized water.

3. Immerse the electrode in pH 7 buffer solution.

4. Adjust the temperature compensator to the sample temperature.

5. Follow directions for 2 point calibration using pH 4 and pH 7 buffer. Record the calibration on the logsheet for the pH meter.

6. Remove the electrode from the buffer and rinse thoroughly with demineralized (deionized) water.

7. Pour a small volume (25 ml- 50 ml) of sample into a beaker and do not immerse the electrode in any sample portion which is being sent to a laboratory for chemical analysis. Immerse the electrode in the unknown solution.

8. Read and record the pH of the solution, after adjusting the temperature compensator to the sample temperature.

9. Rinse the electrodes with demineralized water.

10. Keep the electrode immersed in water, or covered with protective cap filled with pH 7 buffer, at all times when not in use.

11. Prior to each pH measurements, check calibration with pH buffer. Criteria for acceptance = ±0.1 pH units. Also see SOP for Corning Model 103 pH meter.

4.3.2 Indicator Paper

The following procedure is used for measuring pH with pH indicator paper:

1. Immerse a one-inch strip of indicator paper into 25 ml to 50 ml of the unknown solution, immediately withdraw it, or pour a portion of the sample over a small piece of pH paper. Do not allow the indicator paper to contact any sample being sent to a laboratory for chemical analysis.

2. Compare the color of the wet pH paper with the indicator colors given on the pH paper container.

3. Record the pH value which most closely resembles the colors shown. (Note: If the indicator paper is suspected of being old or deteriorated, immerse it in an appropriate buffer and check the color that develops against the standards given. Discard all rolls of deteriorated paper.)

4.4 RECORDS

All results are to be recorded in the field logbook.

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1. OBJECTIVE

This guideline summarizes the steps necessary to use the Corning Model 103 pH meter.

2. LIMITATIONS

This guideline is applicable to all aqueous samples such as potable well water, monitoring well water (groundwater), surface water, wastewater, leachate, and other water samples. Measurements should be taken as soon as possible after sample collection to avoid sample changes which can affect the apparent pH reading.

3. DEFINITIONS

"pH" -- The negative log (base 10) of the hydrogen ion concentration [H+] in a sample.

4. GUIDELINES

4.1 GENERAL

The 103 pH meter is a precision instrument compatible with pH electrodes and is designed for use as a hand-held instrument. The 103 can be used with a 9V battery for portable applications. The digital display provides a direct readout in pH units or absolute millivolts.

4.2 RESPONSIBILITIES

The project team leader or site manager is responsible for determining when conductivity/temperature measurements should be taken in accordance with the site-specific work plans. Generally, field measurements of temperature and conductivity are made whenever an aqueous sample is taken. The field samplers are responsible for taking the measurements and recording and reporting the results.

4.3 OPERATING INSTRUCTIONS

4.3.1 Initial Use

4.3.1.1 Unpacking

Unpack the instrument and check that all items and accessories are present and undamaged. (This should be checked prior to use in the field.) The following items should be present:

-- Model 103 pH meter

-- Combination electrode

-- Slope adjustment tool (approximately 3 inch long black plastic rod with a phillips head screwdriver on one end; the other end is used for slope adjustment)

— Instruction manual

4.3.1.2 Battery Installation/Change

To install the battery, unclip the battery compartment cover (refer to Figure 42-1) and fit the battery connector onto the battery. Place the battery inside the compartment and replace the battery compartment cover.

4.3.1.3 Electrode Installation

Disconnect the shorting plug from the pH socket (see Figure 42-2), and connect the combination electrode.

4.3.2 Instrument Description

4.3.2.1 Display and Controls (refer to Figure 42-3)

Readout: The liquid crystal display will read from 0.00 to 14.00 in pH mode and from -1999 to 1999 in mV mode. A low battery indicator is also integral to the display and will be sent as LO BAT.

O pH mV: Power and mode switch.

CALIBRATE: This control sets the LCD readout to the value of the first calibration buffer, and operates in pH mode only.

cal 2 Δ %: This control compensates for deviations from the theoretical value of the Nernst slope of the electrode. Used to set the second calibration point when carrying out a 2-point calibration. This control operates in pH mode only. The cal 2 Δ % control is accessible via a hole in the connector panel and is adjusted using the slope adjustment tool supplied.

TEMPERATURE: This control compensates for the slope versus temperature characteristics of electrodes and operates in pH mode only.

4.3.2.2 Input/Output Connectors (refer to Figures 42-1 and 42-2)

pH: Standard BNC socket that will accept a wide range of electrodes. A positive millivolt input at this socket results in a positive mV reading on the display. Adjust TEMPERATURE control to the temperature of the unknown solution.

ref (blue): Standard ref. jack socket that will accept a wide range of reference electrodes.

a.c./d.c. Adapter Socket: Socket for the 9V d.c. power supply provided by the a.c./d.c. adapter. (Note: TAMS does not have this accessory.)

Battery Compartment: Rear panel compartment for 9V battery (NE1604 or equal).

4.3.3 Operating Instructions

NOTE: Refer to Section 4.3.1.2 for information on connecting electrodes and to Section 4.3.3.3 for information on recommended operating procedures.

4.3.3.1 pH Measurements

Calibration:

1. Select pH mode.
2. Rinse electrode with pH 7.00 buffer or deionized water.
3. Immerse the electrode in pH 7.00 buffer and adjust TEMPERATURE control to the temperature of the buffer.
4. When the reading stabilizes, adjust the CALIBRATE control to set the display to the value of the buffer.

   NOTE variations in pH values for changes in buffer temperature are shown on Corning buffer solution bottles.
5. For a 2-point calibration, continue with Step 6.

2-Point Calibration

6. Rinse electrode with the second buffer or deionized water.
7. Immerse electrode in the second buffer and adjust TEMPERATURE control to the temperature of the buffer.
8. When the reading stabilizes, adjust the cal 2 Δ % control, with the slope adjustment tool, to set the display to the value of the second buffer.

Measuring Samples

9. Rinse electrode with unknown solution or deionized water.
10. Immerse electrode in the unknown solution and adjust TEMPERATURE control to the temperature of the unknown solution.
11. Allow time for the display to stabilize, then note the reading.
12. Repeat Steps 9 to 11 for further samples.
13. Recalibrate periodically. The frequency will depend on the degree of accuracy required and the condition of the electrode.

4.3.3.2 Absolute mV Measurement

1. Select mV mode.
2. Rinse the electrode with the unknown solution or deionized water.
3. Immerse the electrode in the unknown solution.
4. Allow time for the display to stabilize, then note the reading.
5. Repeat Steps 2 to 4 for further samples.

4.3.3.3 Operating Hints

To make accurate measurements, it is essential that care is exercised when using electrodes.

The following points will help to obtain the optimum performance of the Corning Model 103 pH meter 103 and the electrode system:

1. Conditioning requires that glass pH and combination electrodes are presoaked for at least eight hours in pH 7 buffer solution. Distilled or deionized water is not recommended. As a general rule, the electrode should be stored in a buffered medium around pH 7 and should not be allowed to dry out. A pH electrode with a slope value of less than 50mV per decade should not be used. If the slope value fails rapidly, the pH bulb should be cleaned. Refer to the electrode manufacturer's instructions.
2. Make sure that reference and combination electrodes are filled with the recommended fill solution and that when in use the fill hole cap is removed from the fill hole. Failure to remove it will result in drifting readings because the flow of the fill solution will be impaired.
3. Avoid handling the electrode membrane. Any damage to its surface caused by abrasion will lead to inaccuracy and slow response.
4. Retain the manufacturer's instructions supplied with electrodes, and refer to these for operating, conditioning, storage and maintenance information.
5. Do not use buffer solutions after the expiration date shown on the label and do not pour solutions back into the bottle.
6. When transferring electrodes from one solution to another, the electrode should be rinsed with the solution that is to be measured or deionized water. Then blot the electrode with tissue paper. Do not wipe the electrodes with tissue paper as it may result in slight polarization and consequent sluggishness of response.
7. Response time (i.e., the time required for the electrode to reach equilibrium when transferred from one solution to another) is a function of both the electrode and the solutions. With some solutions, very rapid

equilibration times are possible, while other solutions, particularly those of low ionic strength, may exhibit response times of several minutes.

8. When measuring low ionic strength solutions, either of high or low pH, some drift may be observed. Equilibration times are normally longer in such solutions and greater care should be exercised when taking measurements. To decrease the response time of measurements of distilled or deionized water, one drop of saturated KCl may be added to 50 ml of water sample.

4.4 MAINTENANCE AND PROBLEM SOLVING

4.4.1 Routine Maintenance

The 103 has been designed for a long, troublefree life without the need for regular maintenance. For optimum performance, carry out the electrode maintenance as detailed in the manufacturer's instructions (supplied with the electrode). If required, clean the external casework with a slightly damp cloth — do not use solvents to clean the 103. For information on changing the battery, refer to Section 4.3.1.2.

4.4.2 Instrument Check Procedure

1. Select mV mode.
2. Disconnect the electrode and connect the shorting plug to the pH socket.
3. Check that the display reads between -002 and 002.
4. Select pH mode.
5. Set TEMPERATURE control to 25°C.
6. Check that the display can be set to 7.00 using the CALIBRATE control.
7. Check that the display can be set to 8.00 by clockwise rotation of the CALIBRATE control.
8. Check that the display can be set to 6.00 by counterclockwise rotation of the CALIBRATE control.

4.4.3 Problem Solving

If a fault occurs, it must be isolated to the electrode or the instrument.

For the following faults, carry out the action indicated:

Fault	Action
1. Slow Response Unstable response	Refer to Section 4.3.3., paragraph 7 Condition/substitute electrode. (Refer to electrode manufacturer's instructions.)
2. LO BAT indicated	Replace battery (Refer to Section 4.3.1.2.)
3. Displays blank	Check that pH or mV mode is selected. Check that the battery is fitted correctly or that the a.c./d.c. adapter is connected to the a.c. supply.
4. CALIBRATE control inoperative cal 2 Δ % control inoperative TEMPERATURE control inoperative	Check that pH mode is selected.
5. Display shows: Negative reading or 1 in pH mode, other digits blank -1 or 1 in mV mode, other digits blank	Overrange indicated; check that electrode is connected and immersed in solution. Check that wetting cap has been removed. Substitute connection lead, if used.

4.5 SPECIFICATIONS

Display

Liquid crystal display (LCD), 12.7 mm high.

Operating Ranges

pH
0 to 14.00 pH

Absolute mV
0 to ± 1999 mV

Resolution

0.01 pH : 1 mV

Relative Accuracy

±0.01 pH : ±1 mV, plus one least significant digit

Precision

±1 least significant digit

Input Conditions

Impedance, 10^{12} ohms
Current, typically 1 pA

Drift

±0.01 pH : ±1 mV, plus one least significant digit. Measured over a 24 hour period. Assumes a maximum ambient temperature change of ±4°C and is specified for the instrument only.

Isopotential Point

Set at pH 7.00

Temperature Control Range

0 to 100°C

Power Requirements

Battery, 9 volt (NE 1604) or optional a.c./d.c. adapter (voltage range 90 to 127V a.c.). (TAMS does not have the adapter.)

FIGURE 42-1

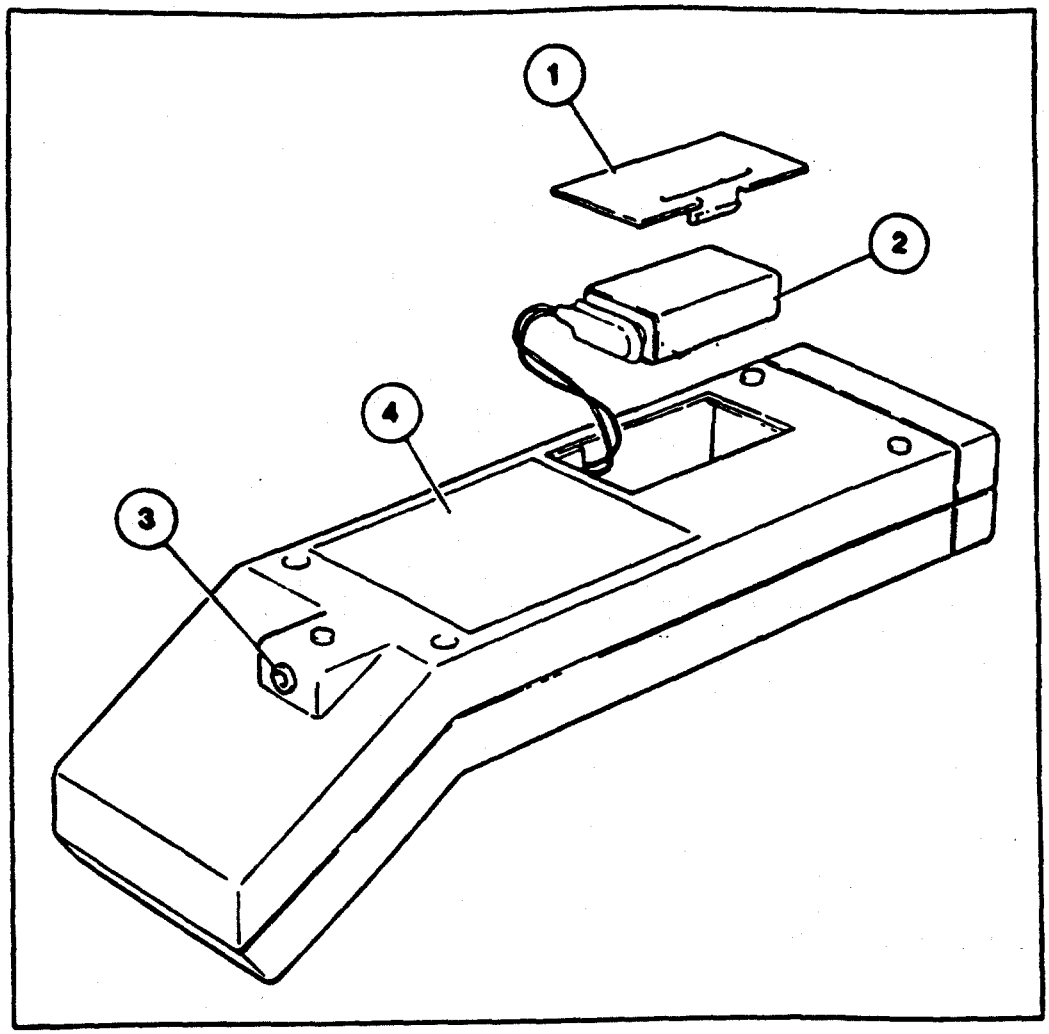

FIGURE 42-1 REAR PANEL

1 - Battery compartment cover
2 - 9V Battery
3 - Socket for a.c./d.c. adapter
4 - Serial number plate

FIGURE 42-2

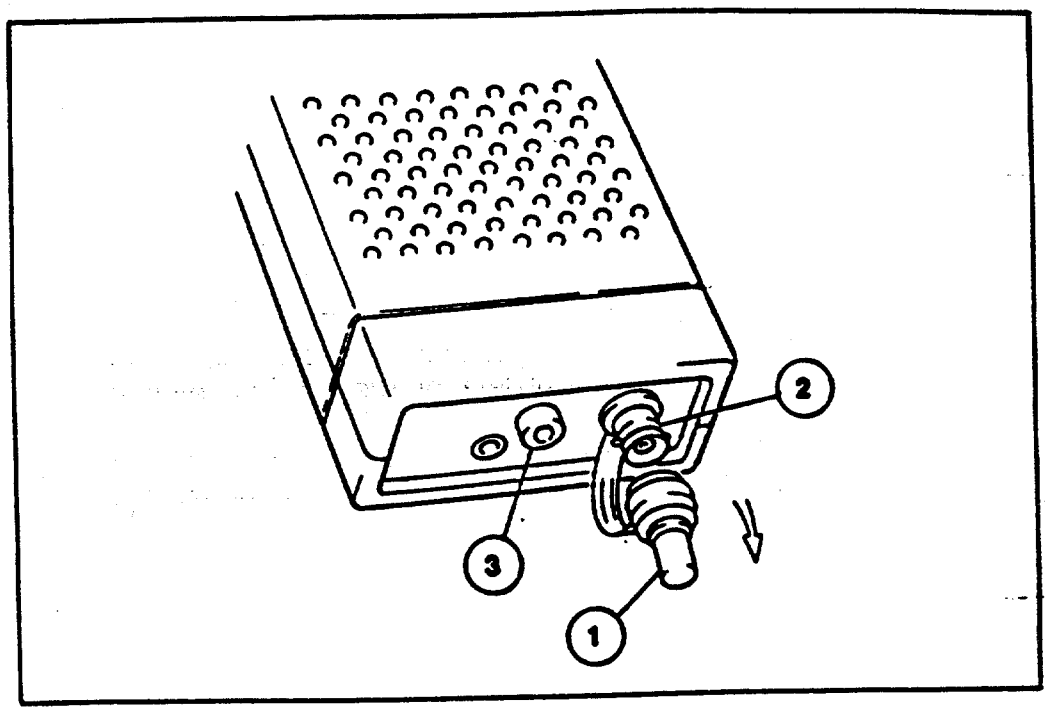

FIGURE 42-2 CONNECTOR PANEL

1 - Shorting plug
2 - pH socket
3 - ref. socket

FIGURE 42-3

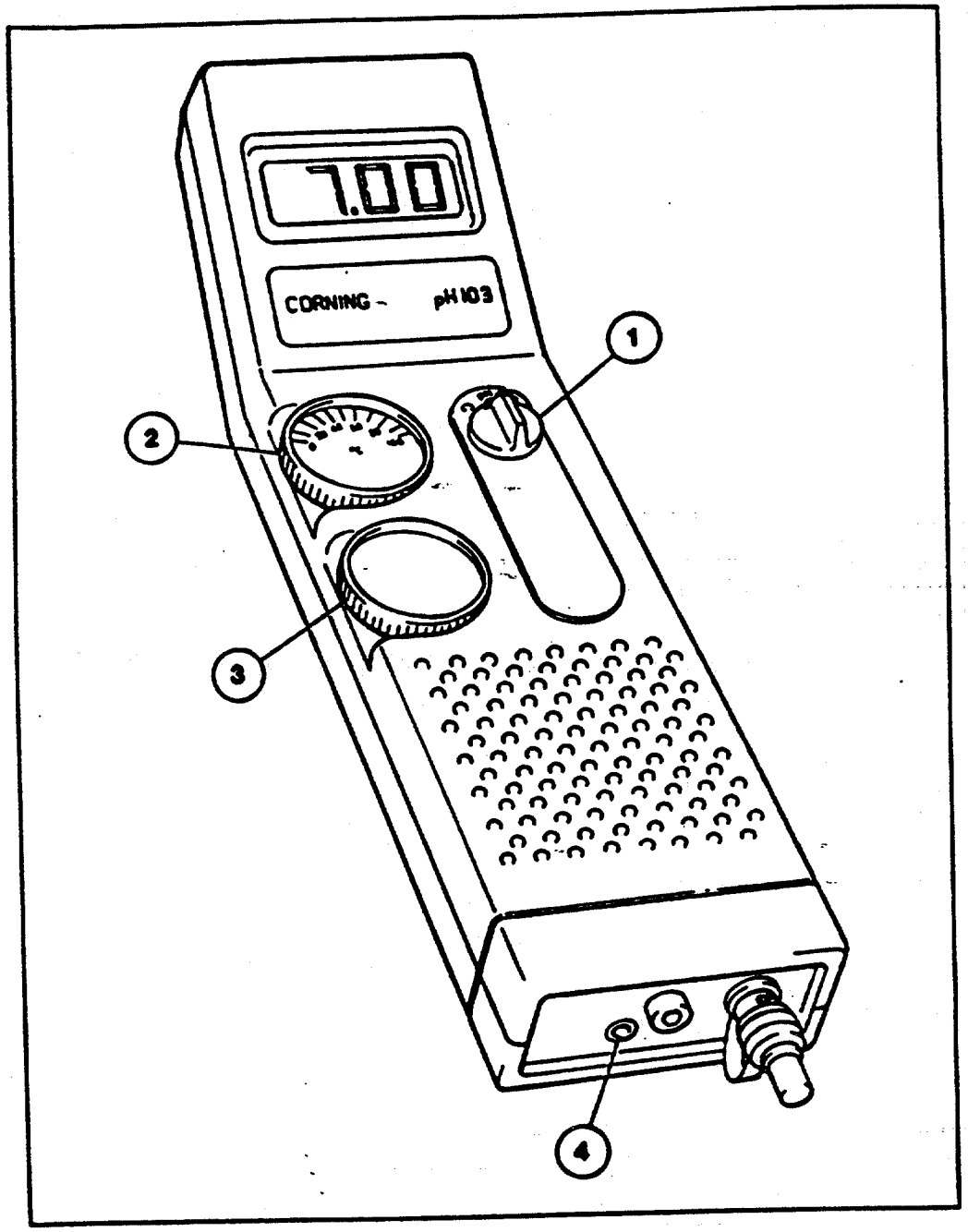

FIGURE 42-3 DISPLAYS AND CONTROLS

1 - Power and mode swithch
2 - TEMPERATURE control
3 - CALIBRATE control
4 - cal 2Δ% control

C-3
Dissolved Oxygen - Field Measurement SOP for Waters

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YSI MODEL 57 DISSOLVED OXYGEN METER STANDARD OPERATING PROCEDURE 38

1. OBJECTIVE

This guidelines summarizes the steps necessary to use the YSI Model 57 Dissolved Oxygen Meter.

2. LIMITATIONS

This guideline is applicable to all aqueous samples. Measurements should be taken as soon as possible after sample collection to avoid sample changes which can affect the apparent DO reading.

3. DEFINITIONS

"Dissolved Oxygen (DO)"--The amount of oxygen dissolved in water.

4. GUIDELINES

4.1 GENERAL

The YSI Model 57 oxygen meter is a precision instrument for measuring dissolved oxygen and temperature in water. The sensing element is a Clark-type, membrane-covered polarographic probe. It is battery-operated and completely portable.

4.2 RESPONSIBILITIES

The project team leader or site manager is responsible for determining when the DO should be taken, in accordance with the site-specific work plans. Generally, field measurement of DO and temperature are made whenever an aqueous sample is taken. The field samplers are responsible for taking the measurements and recording and reporting the results.

4.3 OPERATING INSTRUCTIONS

4.3.1 Initial Use - Preparing the Oxygen Probe

All YSI 5700 series oxygen probes (see specifications) have similar sensors and should be cared for int he same manner. They are precision devices and require good treatment if high accuracy measurements are to be obtained.

The procedure for preparing the probe is an follows (see Figure 38-2):

1. Add distilled water to the KCl crystals and dissolved completely. (Tap water introduces harmful contaminants to the probe.)

2. Transfer a part of the KCl solution to the eyedropper bottle.

3. Remove sensor guard from the probe (YSI 5739 probe).

4. Remove the protective membrane and "O" ring and thoroughly rinse the sensor with KCl solution.

5. Fill the Probe with Electrolyte as follows:

   Grasp the probe in your left hand. When preparing the YSI 5739 probe the pressure compensating vent should be to the right. Successively fill the sensor body with electrolyte while pumping the diaphragm with the eraser end of a pencil or similar soft, blunt tool. Continue filling and pumping until no more air bubbles appear. (With practice you can hold the probe and pump with one hand while filling with the other.) When preparing the YSI 5720A and 5750 probes, simply fill the sensor body until no more air bubbles appear.

   Secure a membrane under your left thumb. Add more electrolyte to the probe until a large meniscus completely covers the gold cathode. NOTE: Handle membrane material with care, keeping it clean and dust free, touching it only at the ends.

   With the thumb and forefinger of your other hand, grasp the free end of the membrane.

   Using a continuous motion stretch the membrane UP, OVER, and DOWN the other side of the sensor. Stretching forms the membrane to the contour of the probe.

   Secure the end of the membrane under the forefinger of the hand holding the probe.

Roll the "O" ring over the end of the probe. There should be no wrinkles in the membrane or trapped air bubbles. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the "O" ring.

Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.

6. Shake off excess KCl and reinstall the sensor guard.

7. A bottomless plastic bottle is provided with the YSI 5739 probe for convenient storage. Place a small piece of moist towel or sponge in the bottle and insert the probe into the open end. This keeps the electrolyte from drying out. The YSI 5720A and 5750 probes can be stored in B.O.D. bottle containing about 1" water.

8. Membranes will last indefinitely, depending on usage. Average replacement is 2-4 weeks. However, should the electrolyte be allowed to evaporate and an excessive amount of bubbles form under the membrane, or the membrane become damaged, thoroughly flush the reservoir with KCl and install a new membrane.

9. Also replace the membrane if erratic readings are observed or calibration is not stable.

10. "Home brew" electrolyte can be prepared by making a saturated solution of reagent grade KCl and distilled water, and then diluting the solution to half strength with distilled water. Adding two drops of Kodak Photo Flo per 100 ml of solution assures good wetting of the sensor, but is not absolutely essential.

11. The gold cathode should always be bright and untarnished. If it is tarnished (which can result from contact with certain gases) or plated with silver (which can result from extended use with a loose or wrinkled membrane), return it to the factory for service or else clean it with the YSI 5680 Probe Reconditioning Kit. Never use chemicals or any abrasive other than that supplied with this kit.

12. It is also possible that the silver anode may become contaminated, which will prevent successful calibration. Try soaking the probe overnight in a 3% ammonia solution; rinse with deionized water, recharge with electrolyte, and

install a new membrane. If still unable to calibrate, return the probe for service.

13. H_2S, SO_2, Halogens, Neon, Nitrous Oxide and CO are interfering gases. If you suspect erroneous readings, it may be necessary to determine if these are the cause. These gases have been tested for response.

100% Carbon Monoxide-Less than 1%	100% Helium-none
100% Carbon Dioxide-Around 1%	100% Nitrous Oxide-1/3 O_2 response
100% Hydrogen-Less than 1%	100% Ethylene-none
100% Chlorine-2/3 O_2 response	100% Nitric Oxide-1/3 O_2 response

4.3.2 Preparing the Instrument

It is important that the instrument be placed in the intended operating position (vertical, titled, or on its back) before it is prepared for use and calibrated. Readjustment may be necessary when the instrument operating position is changed. After preparing the probe proceed as follows:

1. With switch in the OFF position, adjust the meter pointer to Zero with the screw in the center of the meter panel. Readjustment may be necessary if the instrument position is changed.

2. Switch to RED LINE and adjust the RED LINE knob until the meter needle aligns with the red mark at the 31°C position.

3. Switch to ZERO and adjust to zero with zero control knob.

4. Attach the prepared probe to the PROBE connector of the instrument and adjust the retaining ring finger tight.

5. Before calibrating allow 15 minutes for optimum probe stabilization. Repolarize whenever the instrument has been OFF or the probe has been disconnected.

4.3.3 Instrument Description

4.3.3.1 Specifications

1. Instrument

Ranges: 0-5, 0-10, and 0-20 mg/l (0-2.5, 0-5 and 0-10 mg/l with YSI 5776 High Sensitivity Membrane)

Accuracy: ±1% of full scale at calibration temperature (±0.1 mg/l on 0-10 scale), or 0.1 mg/l (whichever is larger).

Temperature Measurement

Range: -5° to +45°C
Accuracy: ±0.5°C plus probe which is ±0.1°C
Readability: 0.25°C

Temperature Compensation: ±1% of D.O. reading for measurement made within ±5°C of calibration temperature; ±3% of D.O. reading over entire range of -5 to +45°C probe temperature.

System Response Time:

Typical response for temperature and D.O. readings is 90% in 10 seconds at a constant temperature of 30°C with YSI 5775 Membranes. D.O. response at low temperature and low D.O. is typically 90% in 30 seconds. YSI 5776 High Sensitivity Membranes can be used to improve response at low temperature and low D.O. concentrations. If response time under any operating conditions exceeds two minutes, probe service is indicated.

Operating Temperature Range:

Instrument and probe operating range is -5° to +45°C. Large ambient temperature changes will result in 2% loss of accuracy unless Red Line and Zero are reset.

Recorder Output:

0 to 114 to 136 mV. Recorder should have 50,000 ohms minimum input impedance.

Power Supply:

The YSI Model 57 is powered by two disposable "C" size carbon zinc batteries (Eveready 935C or equal) providing approximately 1000 hour operation.

2. Probe

Cathode: Gold
Anode: Silver
Membrane: 001" FEP Teflon
Electrolyte: Half saturated KCl
Temperature Compensation (See SPECIFICATIONS, 1. Instrument)

Pressure Compensation Effective 1/2% of reading with pressures to 100 psi (230 ft. sea water)
Polarizing Voltage: 0.8 volts normal
Probe Current: Air at 30°C = 19 microamps nominal
Nitrogen at 30°C = .15 microamps or less

4.3.4 Measurement Procedure

With the instrument prepared for use and, the probe calibrated, place the probe in the sample to be measured and provided stirring.

1. Stirring for the 5739 Probe can best be accomplished with a YSI submersible stirrer. Turn the STIRRER knob ON. If the submersible stirrer is not used, provide manual stirring by raising and lowering the probe about 1 ft. per second. If the 5075A Calibration Chamber is used, the entire chamber may be moved up and down in the water at about 1 ft. per second.

2. Adjust the SALINITY knob to the salinity of the sample.

3. Allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen. Read dissolved oxygen.

4.3.5 Calibration

The operator has a choice of three calibration methods: Winkler Titration; Saturated Water; and Air. Experience has shown that air calibration is quite reliable, yet far simpler than the other two methods. Only the air method is presented here.

Air Calibration

1. Place the probe in moist air. BOD probes can be placed in partially filled (50 mL) BOD bottles. Other probes can be placed in the YSI 5075A Calibration Chamber (refer to the following section describing calibration chamber) or the small storage bottle (the one with the hole in the bottom) along with a few drops of water. The probe can also be wrapped loosely in a damp cloth taking care the cloth does not touch the membrane. Wait approximately 10 minutes for temperature stabilization.

2. Switch to TEMPERATURE and read Refer to Table 38.1 - Solubility of Oxygen in Fresh Water, and determine calibration value.

3. Determine altitude or atmospheric correction factor from Table 38.2.

4. Multiply the calibration value from Table 38.1 by the correction factor from Table 38.2.

   EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table 38-1, the calibration value for 21°C is 8.9 mg/l. From Table 38-2 the correction factor for 1000 feet is about 0.96. Therefore, the correct calibration value is 8.9 mg/l X 0.96 = 8.54 mg/l.

5. Switch to the appropriate mg/l range, set the SALINITY knob to zero and adjust the CALIBRATE knob until the meter reads the correct calibration value from Step 4. Wait two minutes to verify calibration stability. Readjust if necessary.

   The probe is now calibrated and should hold this calibration value for many measurements. Calibration can be disturbed by physical shock, touching the membrane, or drying out of the electrolyte. Check calibration after each series of measurements and in time you will develop a realistic schedule for recalibration. For best results when not in use, follow the storage procedures

recommended for the probes described under probe Maintenance (Section 4.4.1). This will reduce drying out and the need to change membranes.

4.4 MAINTENANCE AND TROUBLESHOOTING

4.4.1 Probe Maintenance

Keep the probe clean and avoid letting the KCl dry in the probe cavity. When changing the membrane, flush out the probe cavity with KCl solution several times. Do not use abrasives to polish the surface of the gold and plastic. Wipe gently with a soft, lint-free cloth (if required).

It should be noted that some other gases can be reduced at the cathode at the polarizing voltage for oxygen. Included are SO_2 and Halogens. H_2S reacts with the metals and poisons the cell. This poisoning can usually be overcome by periodic wiping of the gold surface with a clean, lint-free, coarse cloth or a hard paper. Do not use any form of abrasive. All poisoning shows as tarnish on the gold and polishing should continue until the gold is shiny.

4.4.2 Instrument Maintenance

Model 57 contains two separate circuits: (1) A temperature bridge circuit; and (2) an amplifier for oxygen measurement. The amplifier is a six resistor balanced-feedback amplifier featuring good temperature stability, low voltage power requirements, and long battery life. Current from the oxygen probe develops a voltage across a resistor network which includes a thermistor (kept at O_2 probe temperature). This voltage is applied to the input of the circuit. A portion of the amplifier output is applied to the amplifier input in a standard negative feedback configuration.

4.4.3 Instrument Batteries

The instrument batteries are two "C" size carbon-zinc cells located inside the instrument on the meter end. These should be replaced when the RED LINE know is at its extreme adjustment or at least annually. The amount of remaining adjustment is an indication of the battery condition. the batteries are replaced by removing the screws on the rear cover of the instrument and removing the two batteries at the end of the instrument near the meter. When installing the new batteries the plus (+) end fits into the red washer on the battery holding.

5. SUMMARY OF OPERATING INSTRUCTIONS

5.1 Calibration

A. Switch instrument to OFF and adjust meter mechanical zero.
B. Switch to RED LINE and adjust.

C. Prepare probe for operation, plug into instrument, wait up to 15 minutes for probe to stabilize. Probe can be located in calibration chamber (see instruction manual) or ambient air.
D. Switch to ZERO and adjust.
E. Adjust SALINITY know to FRESH.
F. Switch to TEMP and road.
G. Use probe temperature and true local atmospheric pressure (or feet above sea level) to determine correct calibration values from Table 38.1 and 38.2.

EXAMPLE: Probe temperature = 21°C; Altitude = 1000 feet. From Table 38-1 the calibration value for 21°C is 8.9 mg/l. From Table 38-2 the altitude factor for 1000 feet is approximately .96. The correct calibration value is:

8.9 mg/l X. 96 factor = 8.54 mg/l

H. Switch to desired dissolved oxygen range 0-5, 0-10, or 0-20 and with calibrate control adjust meter to correct calibration value determined in Step G.

NOTE: It is desirable to calibrate probe in a high humidity environment. See instruction manual for more detail on calibration and other instrument and a probe characteristics.

5.2 MEASUREMENT

A. Adjust the SALINITY know to the salinity of the sample.
B. Place the probe and stirrer in the sample and switch and STIRRER control to ON.
C. When the meter has stabilized switch to the appropriate range and read D.O.
D. It is recommended that the instrument be left on between measurements to avoid necessity for repolarizing the probe.

5.3 GENERAL CARE

A. Replace the instrument batteries when unable to adjust to red line. Use two, Eveready No. 935 "C" size or equivalent.

B. In the BATT CHECK position the voltage of the stirrer batteries is displayed on the red 0-10 scale. Do not discharge below 6.0 volts. Recharge for 14-16 hours with YSI No. 5728 charger.

C. Membrane will last indefinitely, depending on usage. Average replacement is 2-4 weeks. Probe should be stored in humid environmental to prevent drying out.

D. Calibrate daily.

TABLE 38-1 - Solubility of Oxygen in Fresh Water

Table I shows the amount of oxygen in mg/l that is dissolved in air saturated fresh water at sea level (760 mmHg atmospheric pressure) as temperature varies from 0° to 45°C.

Table I — Solubility of Oxygen in Fresh Water

Temperature °C	mg/l Dissolved Oxygen	Temperature °C	mg/l Dissolved Oxygen
0	14.60	23	8.56
1	14.19	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.05
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.31
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

Source: Derived from 15th Edition "Standard Methods for the Examination of Water and Wastewater."

TABLE 38-2 - Altitude Correction Factor

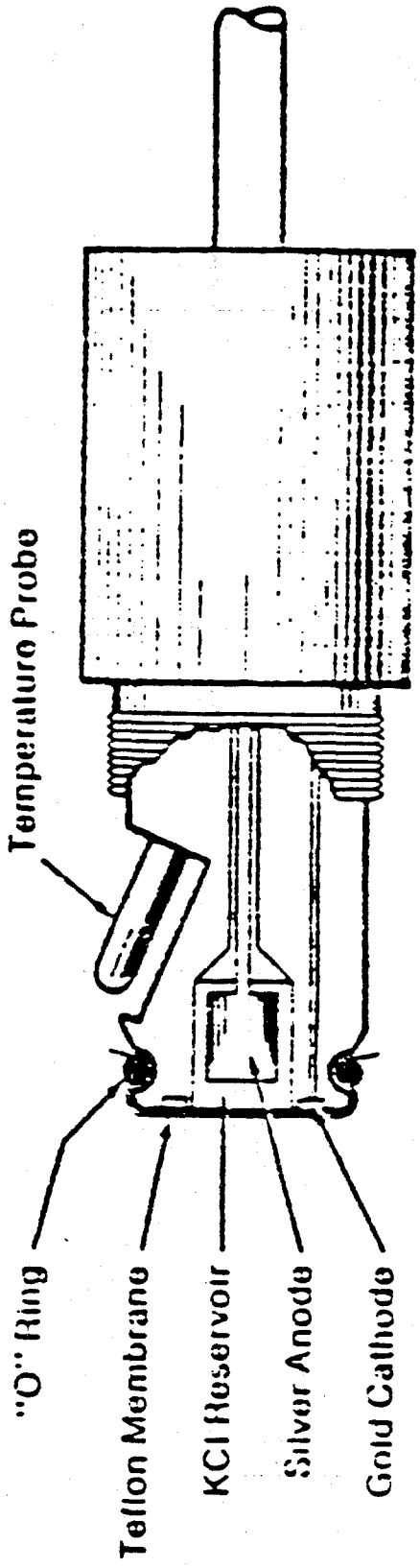
Table II shows the correction factor that should be used to correct the calibration value for the effects of atmospheric pressure or altitude. Find true atmospheric pressure in the left hand column and read across to the right hand column to determine the correction factor. (Note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to seal level.) If atmospheric pressure is unknown, the local altitude may be substituted. Select the altitude in the center column and read across to the right hand column for the correction factor.

Table II — Altitude Correction Factor

Atmospheric Pressure mmHg	or	Equivalent Altitude Ft.	=	Correction Factor
775		540		1.02
760		0		1.00
745		542		.98
730		1094		.96
714		1688		.94
699		2274		.92
684		2864		.90
669		3466		.88
654		4082		.86
638		4756		.84
623		5403		.82
608		6065		.80
593		6744		.78
578		7440		.76
562		8204		.74
547		8939		.72
532		9694		.70
517		10472		.68
502		11273		.66

Source: Derived from 15th Edition "Standard Materials for the Examination of Water and Wastewater."

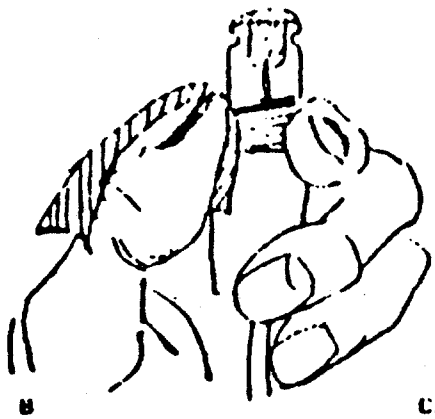
FIGURE 38-1



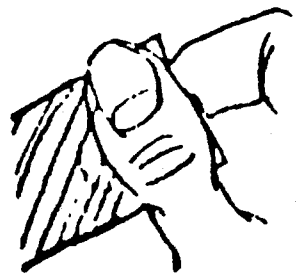
TYPICAL YSI 5400 SERIES O_2/TEMPERATURE ELECTRODE

FIGURE 38-2

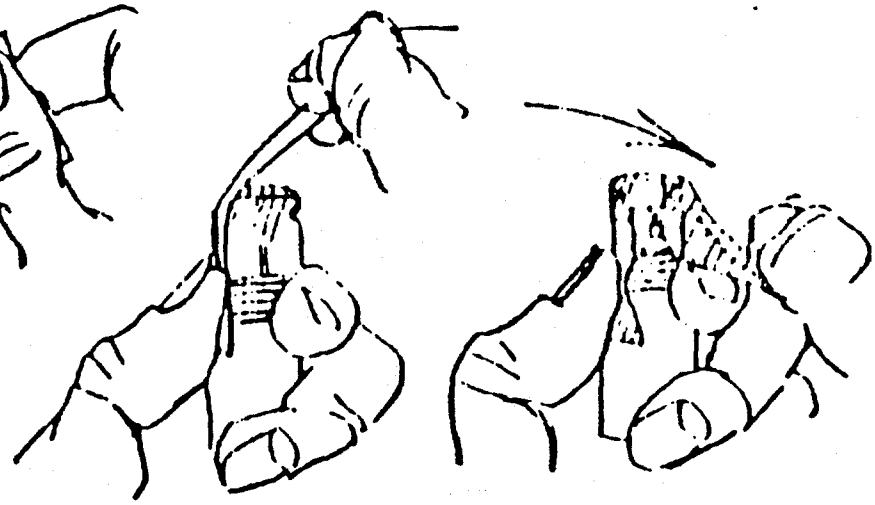
A
Grasp threaded section of probe between left thumb and fore finger.



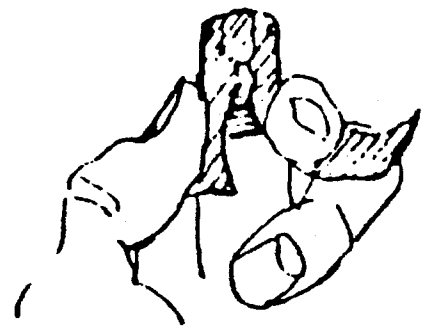
B
Secure one end of membrane under thumb. Use eyedropper to fill probe and wet "O" ring groove with KCl solution.



C.
With right thumb and forefinger grasp free end of membrane.

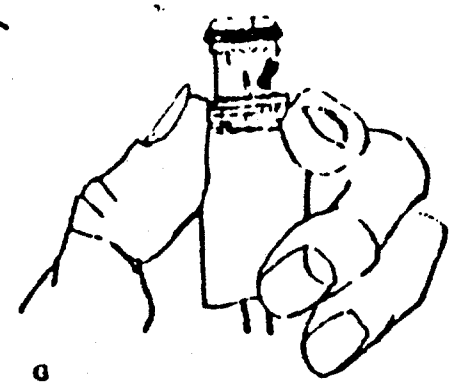


D.
Using a continuous motion stretch the membrane up over down the othe side. Stretching forms the membrane down the sides of the probe.



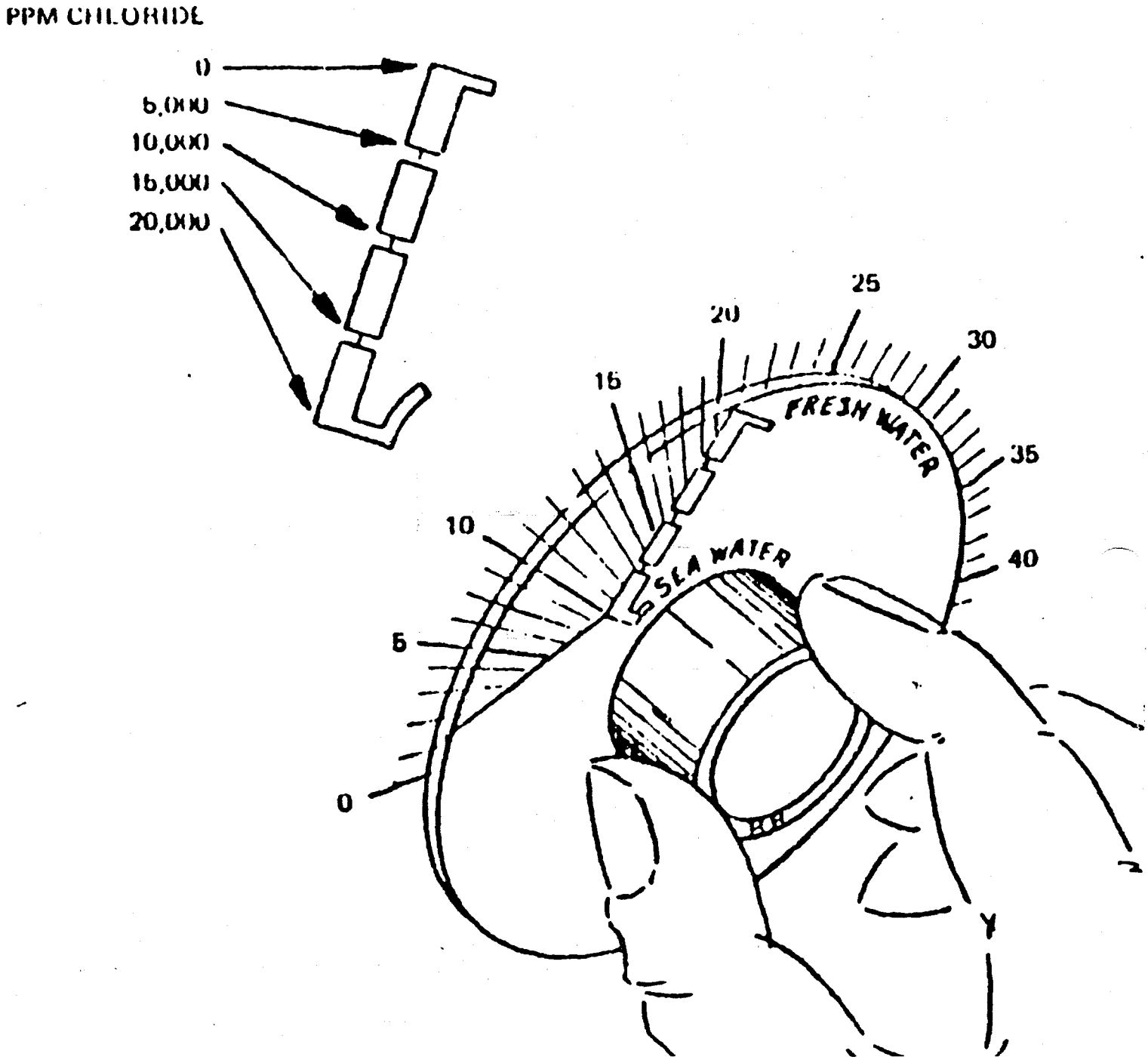
E
Secure the membrane under the left forefinger

F.
Roll on the "O" ring. Inspect to see there are no trapped air bubbles or wrinkles in the membrane.



G
Trim off excess membrane near the "O" ring. Temperature sensor must be exposed for rapid response.

FIGURE 38-3


PPM CHLORIDE
0
5,000
10,000
15,000
20,000
0
5
10
15
20
25
30
35
40
FRESH WATER
SEA WATER

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1. OBJECTIVE

This guideline summarizes the steps necessary to use the YSI Model 33 S-C-T (Salinity, Conductivity, and Temperature) Meter. For this program, conductivity and temperature will be recorded using this instrumentation.

2. LIMITATIONS

This guideline is applicable to all aqueous samples. Measurements should be taken in-situ or as soon as possible after sample collection to avoid sample changes which can affect the readings.

4. GUIDELINES

4.1 GENERAL

The YSI Model 33 S-C-T meter is a portable, battery powered, transistorized instrument designed to accurately measure salinity, conductivity, and temperature. It uses a probe consisting of a plastic conductivity cell and a thermistor temperature sensor combined in a single unit.

4.2 RESPONSIBILITIES

The project team leader or site manager is responsible for determining when the readings should be taken, in accordance with the site-specific work plans. Generally, field measurements of salinity/conductivity and temperature are made whenever an aqueous sample is taken. The field samplers are responsible for taking the measurements and recording and reporting the results.

4.3 OPERATING INSTRUCTIONS

4.3.1 INITIAL USE

4.3.1.1 UNPACKING

Unpack the instrument and check that all items and accessories are present and undamaged. (This should be checked prior to use in the field.) The following items should be present:

- YSI MODEL 33 S-C-T METER
- Combination conductivity/temperature probe

-- Instruction manual

4.3.1.2 **BATTERY INSTALLATION/CHANGE**

To install the battery, unscrew the rear cover and fit the two "D" batteries (alkaline) into the battery holder. Replace the rear cover.

4.3.1.3 **ELECTRODE INSTALLATION**

Connect the probe to the side of the unit.

4.3.2 **INSTRUMENT DESCRIPTION**

4.3.1.2 **DESCRIPTION**

Conductivity

- Ranges: 0 to 500 (x 1), 0 to 5,000 (x 10), and 0 to 50,000 micromhos/cm (x 100). The "micromho" designations on the meter are a shorthand form for "micromhos/cm".

- Accuracy: See Error Section in Manual.

  ±2.5% maximum error at 500, 5,000 and 50,000 plus probe.
  ±3.0% maximum error at 250, 2,500 and 25,000 plus probe.

- Readability: 2.5 micromhos/cm on 500 micromho/cm range.
  25 micromhos/cm on 5,000 micromho/cm range.
  250 micromhos/cm on 50,000 micromho/cm range.

- Temperature Compensation: None.

Temperature Range -2° to +50°C

- Accuracy: ±0.1°C at -2°C, ±0.6°C at 45°C, plus probe error. See Error Section in Manual.

- Readability: 0.15°C at -2° to 3°C at 45°C.

- Power: Supplied by two D-size alkaline batteries. Eveready E95 or equivalent, provide approximately 200 hours of operation.

- Instrument Ambient Range: -5° to +45°C. A maximum error of ±0.1% of the reading per °C change in instrument temperature can occur. This error is negligible if the instrument is readjusted to redline for each reading.

YSI 3000 SERIES CONDUCTIVITY/TEMPERATURE PROBE

- Nominal Probe Constant: K = 5/cm (K = 500/m).

- Accuracy: ±2% of reading for conductivity and salinity. Error of ±0.1°C at 0°C and ±0.3°C at 40°C.

4.3.3 OPERATION

Setup

1. Adjust meter zero (if necessary) by turning the bakelite screw on the meter face so that the meter needle coincides with the zero on the conductivity scale.

2. Calibrate the meter by turning the MODE control to REDLINE and adjusting the REDLINE control so the meter needle lines up with the redline on the meter face. If this cannot be accomplished, replace the batteries.

3. Plug the probe into the probe jack on the side of the instrument.

4. Put the probe in the solution to be measured. (See PROBE Use.)

Temperature

Set the MODE control to TEMPERATURE. Allow time for the probe temperature to come to equilibrium with that of the water before reading. Read the temperature on the bottom scale of the meter in degrees Celsius.

Conductivity

1. Switch to x 100. If the reading is below 50 on the 0-500 range (5.0 on the 0-50 mS/m range), switch to x 10. If the reading is still below 50 (5.0 mS/m), switch to the x 1 scale. Read the meter scale and multiply the reading appropriately. The answer is expressed in micromhos/cm (mS/m). Measurements are not temperature compensated.

Example: Meter Reading	:	247 (24.7 mS/m)
Scale	:	x 10
Answer	:	2470 micromhos/cm (247.0 mS/m)

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C-4
Salinity, Conductivity, and Temperature - Field Measurement SOP for Waters

2. When measuring on the x 100 and x 10 scales, depress the CELL TEST button. The meter reading should fall less than 2%; if greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure.

   Note: The CELL TEST does not function on the x 1 scale.

Conductivity Error

Figure 48-2 shows the worst-case conductivity error as a function of the conductivity reading for the probe and instrument combined.

Example:	Meter Reading	:	360 micromhos/cm (36 mS/m)
	Scale	:	x 10
	% Reading Error	:	±4.5%
	Accuracy	:	3600 ±162 micromhos/cm (360 ±16.2 mS/m) for probe and instrument

Instrument Maintenance

The only maintenance required is battery replacement. Two "D" size alkaline batteries will provide 200 hours of operation. Accuracy will not be maintained if zinc-carbon "D" cells are used. Battery replacement is indicated when the redline adjustment cannot be accomplished.

Replace batteries every six months to reduce the danger of corrosion due to leaky batteries. To replace batteries, remove the screws from the rear cover. The battery holders are color coded. The positive end must go on red.

Recalibration

Recalibration should be done at the factory.

YSI 3300 SERIES CONDUCTIVITY/TEMPERATURE PROBES

Description

These probes are designed and constructed for rugged, accurate service in field use. The conductivity cell constant is 5.0/cm (500.0m) ±2%. Each probe contains a precision YSI thermistor temperature sensor of +0.1°C accuracy at 0°C and ±0.3°C at 40°C. The low capacity cable assembly terminates in a three terminal 0.25 inch diameter phone plug.

Cleaning and Storage

When the cell test indicates low readings, the probable cause is dirty electrodes. Hard water deposits, oils and organic matter are the most likely contaminants.

For convenient normal cleaning, soak the electrodes for 5 minutes with a locally available bathroom tile cleaning preparation such as Lysol Brand "Basin, Tub, Tile Cleaner."

For stronger cleaning, a 5 minute soak in a solution made of 10 parts distilled water, 10 parts isopropyl alcohol, and 1 part HCl can be used.

Always rinse the probe thoroughly in tap water, then in distilled or deionized water after cleaning and before storage.

Caution: Do not touch the electrodes inside the probe. Platinum black is soft and can be scraped off.

If cleaning does not restore the probe performance, replatinizing is required.

Storage

It is best to store conductivity cells in deionized water. Cells stored in water require less frequent platinization. Any cell that has been stored dry should be soaked in deionized water for 24 hours before use.

Replatinization

Return to factory for replatinization.

Probe Use and Precautions

1. Obstructions near the probe can disturb readings. At least two inches of clearance must be allowed from non-metallic underwater objects. Metallic objects such as piers or weights should be kept at least six inches from the probe.

2. Weights are attached to the cable of the YSI 3310 and 3311 probes. The YSI 3327 weights are supplied in pairs with a total weight of 4 ounces per pair. Should it become necessary to add more weight to overcome water currents, limit the total weight to two pounds (8 pairs). For weights in excess of two pounds, use an independent suspension cable. In either case, weights must be kept at least six inches away from the probe.

3. Gentle agitation by raising and lowering the probe several times during a measurement improves flow of specimen solution through the probe and improves the time response of the temperature sensor.

Conductivity and Salinity Corrections for Long Cables

The additional length of wire in long cables adds capacitance and resistance which will affect readings. The recommended way to correct for this influence is by the use of YSI Conductivity Calibrator Solutions which will permit an estimate of correction factors.

Cell Calibration and Standard Solutions

The cell constant of a conductivity cell may vary slightly with the conductivity of the solution being measured. Cell calibration may also be affected by electrode fouling, replatinization, or by mechanical shock. A cell and meter can be calibrated together, as a system with conductivity calibrator solutions.

YSI conductivity calibrator solutions are supplied with a technical discussion and instructions for use. Directions for calibration at temperatures other than 25° are included with the conductivity calibration solutions. In calculating the cell constant in absolute terms, the uncertainty of the meter calibration must be added to the tolerance of the conductivity calibrator solution.

FIGURES 48-1

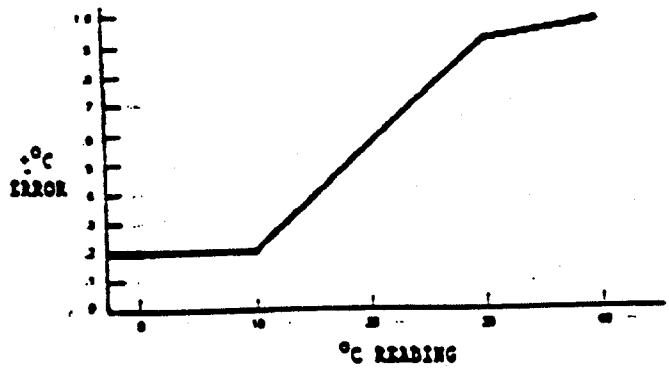


FIGURE 48-2

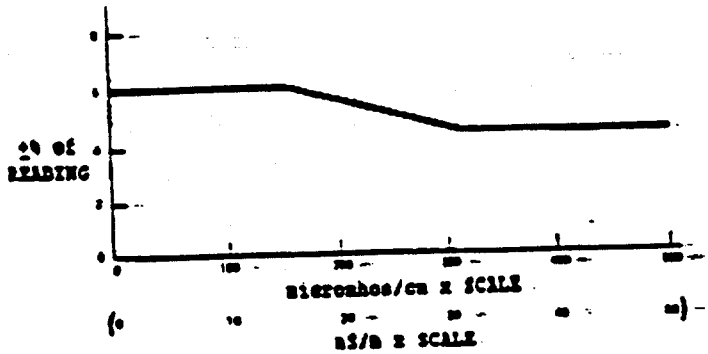
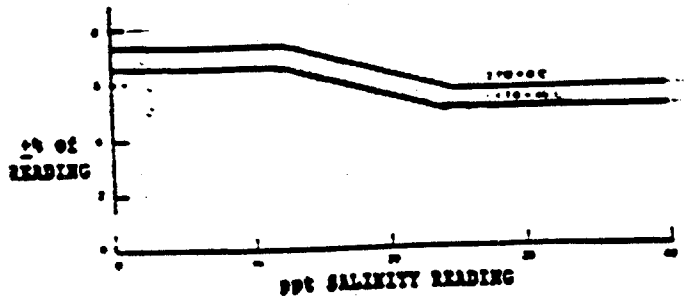


FIGURE 48-3



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C-5
Field PCB Screening

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APPENDIX C-5
PCB RISC® POLYCHLORINATED BIPHENYLS SOIL TEST
TECHNICAL GUIDE

Polychlorinated Biphenyls

Polychlorinated biphenyls are aromatic compounds, based on biphenyl, that have been chlorinated to varying degrees. They are relatively viscous liquids at room temperature. PCBs with higher levels of chlorination are quite stable to oxidation at elevated temperatures and as a result were useful as heat transfer agents. PCBs are a very nearly ubiquitous environmental contaminant due to their use as an insulating and heat transfer fluid in electrical utility equipment. For decades PCBs were the material of choice for utility transformers and load factor capacitors. In addition, PCBS were used in small motor capacitors (machinery and household appliances), large compressors, and chemical process equipment. In all of these applications they were valued primarily for their chemical oxidative stability. Ironically, this property is also responsible for their environmental recalcitrance.

PCBs were sold as complex mixtures of chemically distinct chlorinated species (congeners) under the commercial name Aroclor®. A four digit number, such as 1260, denoted the average number of carbons per molecule (12) and the chlorine content in weight percent (60) of the specific Aroclor.

Existing Laboratory Methods

The laboratory method usually employed for PCB analysis of soil sample extracts is a gas chromatography method (EPA method 8080 or similar). Although it is relatively inexpensive ($90-$150) as organic methods go, it still suffers from the same laboratory turnaround time requirements (2-4 weeks) as other lab methods. Minimum detection limits for the GC method can be quite low (10 ppb), but a laborious cleanup protocol is usually necessary to achieve this detection limit in soil samples. The detection level more often quoted is of the order of 0.5 ppm.

Existing Field Methods

Few fields methods other than the PCB RISC® Soil Test are available to determine PCBs in soil. The other field methods suffer from inadequate sensitivity for PCBS, rendering them inadequate at the lowest concentrations ($\leq$1 ppm).

Test Characteristics

The PCB RISC® Soil Test serves as a field-based alternative to sending all soil samples for analysis by laboratory-based methods. It is semi-quantitative test that gives an absence/presence indication around one or two user chosen detection levels. For example, on a site with the cleanup criterion set to 10 ppm the user might chose to test at 10 ppm or if more information about contamination gradients were needed, test at 10 ppm and 50 ppm. The test is relatively simple to use and allows for the testing of up to 10 samples in one test period. The testing of one sample requires about 30 minutes, while 10 samples can be tested in about 75 minutes.

The PCB test exhibits recognition of all commercial Aroclors. The test was designed to be most sensitive to the most common Aroclors: 1248, 1254, and 1260. The Aroclor sensitivities vary from 0.4 ppm for Aroclors 1254 and 1260 to 4 ppm for Aroclors 1232 and 1016 (Table 1). The sensitivity to other halogenated compounds is generally very small (< 1 % of the response to Aroclor 1260), showing that chemical compounds other than PCBs are unlikely to present problems with false positive results.

Regulatory Status

The PCB RISC® Soil Test conforms to EPA SW-846 Method 4020 for screening for PCBs using immunoassay detection. The EnSys test was the basis for the draft method and it is the only test kit for which data have been submitted and favorably reviewed by the Office of Solid Waste Organic Methods Work Group.

Correlation with Laboratory Methods

The PCB soil test can provide a high degree of accuracy when used to analyze soils contaminated with PCBs. Product validation studies indicate that the test can correctly identify over 95 % of samples that are spiked with PCBs at or above the chosen action level. The recovery of PCBs from spiked soils was independent of the soil used.

Data obtained in the field using the PCB RISC® Soil Test has shown excellent correlation with laboratory analysis for split samples. The data typically show 80 % to 95 % correlation with confirmatory laboratory analyses. Non-correlating results are usually manifested as false positives on the part of the immunoassay, rather than false negatives. This performance is intentionally designed into the test by EnSys in order to ensure that a negative result does not result in the misrepresentation of contaminated soil as clean.

Field Application

The operational temperature range for use in the field with full performance as described above is 40°F to 90°F.

Up to 12 tubes can be run in one batch, so that several samples can be tested concurrently. The shelf life of the PCB RISC® Soil Test is currently 6 months, with longer shelf life expected when the real-time data is available.

Rather than sending every sample to the laboratory for analysis, samples can be analyzed in the field to provide real-time information about PCB levels to guide further sampling or excavation. The appropriate use of field testing can result in substantial savings in project cost due to more efficient use of project resources. All results from field analysis of soil samples using the PCB test should be accompanied by supporting QA data. At the least, method and soil blanks and a performance evaluation sample should be tested daily. In addition, one duplicate sample should be tested for every twenty samples analyzed. Confirmation of a portion of the field results should also be obtained by Method 8080.

Due to the differences in sensitivity to the various Aroclors, care must be taken in selecting the detection level for sites in which mixed Aroclor contamination is present. For example, if a site were contaminated with Aroclors 1242 and 1254, the Field Operations Leader or Quality Control Coordinator would have to decide whether the PCB RISC® Soil Test should be configured to measure Aroclor 1242 at the site action level and expect some false positive due to Aroclor 1254 or to measure Aroclor 1254 at the action level and expect a few false negatives due to Aroclor 1242. The relative concentrations of the two Aroclors in the soil at the site also has a bearing on the decision.

Table 1
PCB RISc® Soil Test Sensitivity

Compound or Substance	Concentration Necessary to Result in Positive Test (ppm)
Polychlorinated Biphenyls	
Aroclor 1260	0.4
Aroclor 1254	0.4
Aroclor 1248	1
Aroclor 1242	2
Aroclor 1016	4
Aroclor 1232	4
Other Halogenated Compounds	
2,4,6-trichloro-*p*-terphenyl	>10000
Halowax 1013	10000
Halowax 1051	1000
o,p-DDT	>10000
2,4-D	10000
Silvex	1000
bifenox	1000
tetradifon	100
diclofop methyl	1000
dichlorofenthion	10000
trichloroethylene	>10000
1,2,4-trichlorobenzene	10000
2,4-dichloro-1-naphthol	50
2,4-dichlorophenyl benzene sulfonate	1000
1-chloronaphthalene	>10000
pentachlorobenzene	>10000
hexachlorobenzene	>10000
2,5-dichloroaniline	>10000
Micellaneous Compounds and Substances	
toluene	>10000
naphthalene	>10000
DIALA(R) Oil AX	>10000
R-Temp fluid	>10000
Envirotemp 200 fluid	>10000
diesel fuel	>10000
gasoline	>10000

11/92

Table 2
PCB RISc® Soil Test Correlation
Gas Pipeline Soils

Sample ID	GC Result (ppm)	5 ppm Test Result	5 ppm Test Evaluation	50 ppm Test Result	50 ppm Test Evaluation
238-001	<0.2	<5	•	<50	•
570-008	<0.2	<5	•	<50	•
327-001	<0.2	<5	•	<50	•
327-002	<0.2	<5	•	<50	•
327-003	<0.2	<5	•	<50	•
327-004	<0.2	<5	•	<50	•
294-002	1	<5	•	<50	•
428-005	2	≥5	FP	<50	•
915-017	4	≥5	FP*	<50	•
296-008	7	≥5	•	<50	•
253-005	11	≥5	•	<50	•
169-005	11	≥5	•	<50	•
982-005	14	≥5	•	≥50	FP
569-010	21	≥5	•	<50	•
250-009	26	≥5	•	≥50	FP
169-006	38	≥5	•	<50	•
296-002	42	≥5	•	≥50	FP*
915-005	43	≥5	•	≥50	FP*
915-015	52	≥5	•	≥50	•
295-004	55	≥5	•	<50	FN*
587-016	72	≥5	•	≥50	•
569-012	73	≥5	•	≥50	•
584-023	75	≥5	•	≥50	•
585-006	75	≥5	•	≥50	•
250-001	77	≥5	•	≥50	•
569-011	79	≥5	•	≥50	•
934-009	130	≥5	•	≥50	•
169-003	240	≥5	•	≥50	•
982-003	350	≥5	•	≥50	•
982-002	710	≥5	•	≥50	•

• - immunoassay and GC agree
FP - false positive
FP* - false positive, but within 25% of GC value
FN* - false negative, but within 25% of GC value

11/92

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

6.2 Soils samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

7.1 Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance indicated in Tables 2-4.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly where results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other kits.

8.5 Use the test kits within the specified storage temperature and operating temperature limits.

8.6 Method 4020 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 A study was conducted using fourteen standard soils and three soil samples where PCB concentration had been established by Method 8080. Replicates were performed on seven of the standard soils and on one of the soil samples for a total of 25 separate analyses. Each of two different analysts ran the 25 analyses. Results indicated that "<" assignments are accurate with almost 99% certainty at the 5 ppm level while ">" assignments can be up to about 96% accurate as the sample concentration approaches that of the testing level. Corresponding certainties at the 5 ppm level are 92% and 82% respectively. Tables 2 and 3 summarize these results.

10.0 REFERENCES

1. J.P. Mapes, T.N. Stewart, K.D. McKenzie, L.R. McClelland, R.L. Mudd, W.B. Manning, W.B. Studabaker, and S.B. Friedman, "PCB-RISc™ - An On-Site Immunoassay for Detecting PCB in Soil", Ensys Inc., Research Triangle Park, NC 27709

2. PCB RISc™ Users Guide, Ensys Inc.

3. R.W. Counts, R.R. Smith, J.H. Stewart, and R.A. Jenkins, "Evaluation of PCB Rapid Immunoassay Screen Test System", Oak Ridge National Laboratory, Oak Ridge, TN 37831, April 1992, unpublished

Table 3
EPA Application of PCB RISc® Soil Test
in Florida

Sample ID	5 ppm Test Result	5 ppm Test Evaluation	50 ppm Test Result	50 ppm Test Evaluation	GC Result (ppm)
17	≥ 5	FP	< 50	•	3.4
19	≥ 5	FP	< 50	•	2.0
20	≥ 5	•	≥ 50	•	68
21	≥ 5	•	≥ 50	•	390
22	≥ 5	•	≥ 50	•	290
23	≥ 5	•	≥ 50	•	66
25	≥ 5	•	≥ 50	FP	16
30	≥ 5	•	≥ 50	•	330
31	≥ 5	•	≥ 50	•	66
33	≥ 5	FP*	< 50	•	4.3
53	< 5	•	< 50	•	0.12
54 (off-site)	< 5	•	< 50	•	0.003

• - Immunoassay and GC results agree
FP - False positive
FP* - False positive but within 25% of GC results

11/92

METHOD 4020

SOIL SCREENING FOR POLYCHLORINATED BIPHENYLS BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4020 is a procedure for screening soils to determine when total polychlorinated biphenyls (PCBs) are present at concentrations above 5 mg/Kg. Method 4020 provides an estimate for the concentration of PCBs by comparison with a standard.

1.2 Using the test kit from which this method was developed, 95 % of samples containing 0.625 ppm or less of PCBs will produce a negative result in the 5 ppm test configuration.

1.3 In cases where the exact concentration of PCBs are required, quantitative techniques (i.e., Methods 8080/8081) should be used.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed. In general, the method is performed using an extract of a soil sample. Sample and an enzyme conjugate reagent are added to immobilized antibody. The enzyme conjugate "competes" with PCBs present in the sample for binding to immobilized anti-PCB antibody. The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standard(s) simultaneously.

3.0 INTERFERENCES

3.1 Chemically similar compounds and compounds which might be expected to be found in conjunction with PCB contamination were tested to determine the concentration required to produce a positive test result. These data are shown in Table 1.

4.0 APPARATUS AND MATERIALS

4.1 PCB Specific Test Kit (EnSys, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

5.1 Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

Table 1 Possible Soil Interferences*	
Compound	Soil Equivalent Concentration (ppm) Required to Yield a Positive Result
1-Chloronaphthalene	10,000
1,2,4-Trichlorobenzene	10,000
2,4-Dichlorophenyl-benzenesulfonate	1000
2,4-Dichloro-1-naphthol	>10,000
Bifenox	
Diesel fuel	,000
Pentachlorobenzene	,000
2,5-Dichloroaniline	>10,000
Hexachlorobenzene	,000
Gasoline	10,000
Dichlorofenthion	10,000
Tetradifon	125

* Ensys, Inc. publication

Table 2
Estimated Error Rates for 5 ppm Dilution

True Value (ppm)	0	1	2	3	4	5	6	7	8	9	10	20
Estimated Rate of False Positives (%)	1.3	13.2	39.2	65.2	82.3	-	-	-	-	-	-	-
Estimated Rate of False Negatives (%)	-	-	-	-	-	8.5	4.1	2.0	1	0.5	0.3	<0.1

Table 3
Estimated Error Rates for 50 ppm Dilution

True Value (ppm)	0					30	40	50	60	70	80	100
Estimated Rate of False Positives (%)	1.0	7.9		46.0	65.0	87.3	95.6	-	-	-	-	-
Estimated Rate of False Negatives (%)	-			-	-	-	-	1.7	0.7	0.3	0.2	<0.1

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APPENDIX D

QUALITY ASSURANCE AUDITS

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D-1
Field Quality Assurance Audits

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Appendix D-1

Field Quality Assurance Audit

Program: Hudson River Phase 2B - Benthic and Sediment Sampling

Date of Audit: _____

Audit Conducted By: _____

On-Site Sampling Personnel: _____

_____

_____

Audit Conducted on the Following:

_____ Sediment Sampling (Grab)

_____ Benthic Organism Sampling

_____ Decontamination Procedures

_____ Sample Handling, Labeling, Aliquoting Procedures

Y = Yes N = No N/A = Not Applicable N/D = Not Determined

I. Overall Sample Collection

		Yes	No
1.	Do sampling locations agree with those specified in the SAP/QAPjP?		
2.	Is the sampling location either documented sufficiently or marked to allow it to be found/sampled again in the future?		
3.	Are sampling times, Traffic Report Numbers and sample description noted in the Field Note Book (FNB)?		

		Yes	No
4.	Have all field measurements been properly taken as per Sampling Plan? • pH • conductivity/temperature • dissolved oxygen • PCB screening • salinity		
5.	Have sample bottles been labeled properly?		
6.	Have proper containers and preservatives been used?		
7.	Are proper sample volumes procured?		
8.	Have sampling times been recorded in order to complete documentation on holding times per sample per parameter?		
9.	Have weather conditions been recorded?		
10.	Have MS and MSD(s) and MD(s) been collected as per SAP/QAPjP frequencies?		
11.	Have field blanks been collected as per SAP/QAPjP frequencies?		
12.	Have field duplicates been collected as per SAP/QAPjP frequencies?		
13.	Are samples being refrigerated/iced immediately after collection?		
14.	Has condition of sample been recorded in the FNB and in the traffic report?		
15.	Does the potential for sample cross-contamination exist based on procedures observed?		
16.	Have samples been properly packaged and labeled for shipment to appropriate laboratory for analysis?		

	Yes	No
17. Have legal seal(s) been properly filed out and attached to the shipping containers?		
18. Has the Chain-of-Custody Form been properly filled out and a copy included with sample shipments?		

II. Sediment Sampling

1. Type: core _____ If core, state type: gravity core _____
hand core _____
vibracore _____

grab _____

	Yes	No
2. Is a description of sediment cores being logged?		
3. Have sediments been homogenized where applicable prior to aliquoting (specified by the Sampling Plan)?		
4. Are proper slicing/aliquoting procedures being followed as per QAPP?		
5. Has Redox been measured as per QAPP?		

Comments:

III. River Water Sampling

	Yes	No
1. Are PCB samples collected directly into precleaned bottles?		
2. Are samples for dissolved or particulate analyses filtered within 4 hours of collection?		
3. Are filtering procedures being followed as per QAPP?		
4. Are dissolved organic carbon samples being filtered and preserved?		
5. Are chlorophyll a samples being filtered and the filter properly placed in container for analysis?		
6. Are field pH, conductivity, and temperature and dissolved oxygen being measured and documented? Is there documentation of calibrating the instruments?		

Comments:

IV. Decontamination Procedures

		Yes	No
1.	Have all sampling materials (spatulas, spoons, etc.) and equipment (e.g. filter apparatus) been decontaminated properly for the given analytes as per QAPP?		
2.	Have the proper decontamination solutions been used?		
3.	Has decontamination water/solution been collected for proper disposal?		
4.	Has disposable equipment that is contaminated been properly deconned and disposed of?		
5.	Have decon samples been taken from the sampling equipment as per Sampling Plan?		

Comments:

V. General

	Yes	No
1. Has all appropriate information been recorded in the FNB?		
2. Are employees conducting the investigation in a professional manner?		
3. Are the objectives of the sampling activities understood by the field personnel?		
4. Are weather conditions affecting sample quality?		

Comments:

Audit Summary and Comments:

Signed by:

Sampler: _____ Print Name: _____

Auditor: _____ Date: _____

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D-2
Laboratory Quality Assurance Audits

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Gradient Corporation

Laboratory Being Audited: _____

Date of Audit: _____

Audit Conducted By: _____

Laboratory Evaluation Checklist

I. Orientation Meeting

A. Organization and Personnel

1. Laboratory or Project Manager (individual responsible for overall technical effort): _____

2. Inorganic Laboratory Supervisor (BS or BA in science and 3 years related experience, including 1 year as a supervisor): _____

3. Organic Laboratory Supervisor (BS or BA in science and 3 years experience including 1 year as a supervisor): _____

4. Analyst(s) for Inorganic analyses (BS or BA in science and 1 year direct experience for each technique or instrumental analysis): _____
_____

5. Analyst(s) for Organic Analyses (BS or BA in science and 1 year direct experience for each technique or instrumental analysis): _____
_____

6. Inorganic Sample Preparation Specialist(s) (High School Diploma and college level course in chemistry and 6 months related experience): _____
_____

7. Organic Sample Preparation Specialist(s) (High School Diploma and college level course in chemistry and 6 months related experience): _____
_____

8. Back-up Technical Personnel (BS or BA in science and 1 year experience in each technique or instrumental analysis including: GC, classical wet chemistry techniques, biological properties, radiochemistry, geophysical properties as applicable to the program): _____
_____
_____

9. Quality Assurance Director: _____

10. Glassware Preparation Technician: _____

11. Sample Custodian: _____

12. Is the organization adequately staffed to meet project commitments in a timely manner? _____

13. Are resumes for all listed personnel available? Do the resumes demonstrate that the personnel meet education and experience requirements? _____

_____

14. Were all key personnel available during the on-site visit? _____

15. To whom does the QA Officer report? Senior Management?

_____

B. Documentation

1. Is the written QA Manual available and satisfactory for the following:

Personnel	_____
Facilities and equipment	_____
Operation of instruments	_____
Documentation of procedures	_____
Preventive maintenance	_____
Reliability of data	_____
Feedback and corrective action	_____
Archival of outdated SOPs	_____

Comments:

2. Are written SOPs available and satisfactory for the following?

Receipt and storage	_____	Data package preparation	_____
Security	_____	Standards preparation	_____
Glassware cleaning	_____	Technical review of data	_____
Sample preparation	_____	Instrument maintenance	_____
Analytical methods	_____	QA/QC self inspection	_____

Comments:

II. Laboratory Tour - When touring facilities, give special attention to: (a) the overall appearance of organization and neatness, (b) the proper maintenance of facilities and instrumentation, (c) the general adequacy of the facilities to accomplish the required work.

A. Sample Receipt and Storage Area

	Yes	No
1. Is the sample receiving area secure?		
2. Are coolers opened in a contamination free area (preferably in a functional hood)?		

		Yes	No
3.	Does the observed sample log-in procedure agree with the written SOP?		
4.	Is the appropriate portion of the SOP available to the Sample Custodian? Is the temperature of the cold storage recorded daily?		
5.	Are adequate facilities provided for storage of samples, including cold storage?		
6.	Are the sample receipt/storage and temperature records maintained in a manner consistent with good laboratory practice (GLP)?		
7.	Is there a periodic document review by the supervisor?		

Comments:

B. Preparation Area

1. General Operation	Yes	No
a. Does the laboratory appear to have adequate workspace (120 sq. feet, 6 linear feet of unencumbered bench space per analyst)?		
b. Is the laboratory maintained in a clear and organized manner that is appropriate for trace level analysis?		
c. Are the hoods functional and periodically checked?		
d. Does the laboratory have source of distilled/ demineralized water and is the water quality routinely checked and documented?		
e. Is the analytical balance located away from drafts and areas subject to rapid temperature changes?		
f. Has the balance been calibrated within 1 year by a certified technician?		
g. Is the balance routinely checked with the appropriate range of class S weights before use and are the results recorded in a logbook?		
h. Is an adequate drying oven available with a temperature measurement device? Is the temperature being monitored?		

Comments:

2. Glassware Washing — Yes — No

a. Is the SOP for glassware washing posted and is it followed by the technician(s)?

b. Does the SOP prescribe an adequate amount of acid or solvent treatment of the glassware and DI water rinses?

Comments:

3. Standards Preparation — Yes — No

a. Is the appropriate SOP available in the area for preparation and traceability?

b. Are unexpired standards used to prepare instrument calibration standards? Are standards dated upon receipt?

c. Are fresh analytical standards prepared at a frequency consistent with good QA?

		Yes	No
d.	Are standards properly labeled with concentrations, date of preparation, date of expiration, and the identity of the person preparing the standard?		
e.	Is the reference/spiking/ calibration standards preparation and tracking logbook(s) maintained?		
f.	Does the laboratory use automatic pipets for preparing their standards? If yes, are these pipet calibrated on a routine basis?		
g.	Are reagent grade or higher purity chemicals used to prepare standards?		
h.	Are the primary standards traceable to EPA reference standards?		

Comments:

4.	Sample Preparation Area	Yes	No
a.	Is the Sample Preparation SOP available in the area? Do the procedures followed by the analyst agree with those documented in the SOP?		
b.	Are the digestion logbooks/bench sheets maintained in a manner consistent with the QAPP or contractual requirements?		
c.	Is the pH of the samples recorded and available for data review?		
d.	Are standards stored separately from the digestates or extracts?		
e.	Do the digested/extracted sample batches examined contain method blanks, LCSs, duplicates, and matrix spikes where applicable for inorganic parameters? Contain LCS, MS, MSD, method blanks for organic parameters? List SDG# examined in Audit: _____		
f.	Are the samples measured and transferred to the beakers or extraction vessels as per method SOP (by volume, weight, etc.)?		
g.	Is a consistent procedure used for transferring the sample numbers from the sample bottles to the extraction/digestion beakers or vials?		
h.	Is the QC digested/extracted with the samples?		

		Yes	No
i.	Can the laboratory supervisor document that organic-free water or inorganic analyte free water is available for preparation of standards and blanks? (Method blank data must be available for confirmation.)		
j.	Are solvent storage cabinets vented or located in such a way as to prevent possible laboratory contamination? (Confirm by method blank data.)		

Comments:

		Yes	No
k.	Are analytical reagents dated upon receipt?		
l.	Are solvents and acids and other reagents used in preparations checked routinely per lot number received by vendor prior to routine use in the lab?		
m.	Are the temperatures of the refrigerators/freezers recorded daily?		

		Yes	No
n.	Are temperature excursions noted and appropriate actions taken when required?		

Comments:

C.	Sample Analysis Instrumentation	Yes	No
1.	Are manufacturer's operating manuals readily available to the operators?		
2.	Are extensive in-house replacement parts available? Does the laboratory maintain a service contract?		
3.	Is a permanent service maintenance record maintained in a logbook? For routine, and non-routine maintenance?		
4.	Is the instrument properly vented or are appropriate traps in place?		
5.	Is raw data being archived properly (i.e. magnetic tape storage)?		
6.	Is a log of the contents of the raw data magnetic tapes available?		

		Yes	No
7.	Can the instrument operator demonstrate, using the instrument run log, that corrective actions have been taken when required (e.g., reruns)?		
8.	Are reruns performed when internal standard areas are out?		
9.	Are analytical blanks run when the previous sample showed saturation?		
10.	Has two column verification of PCB congeners been performed?		

Comments:

III. Data Handling and Review

		Yes	No
1.	Does the laboratory analyst perform a primary review of the data as stated in the program QAPP?		
2.	Are data calculations spot-checked by a secondary reviewer?		
3.	Do records indicate that appropriate corrective action has been taken when analytical results fail to meet QC criteria?		
4.	Are computer programs validated before use?		

	Yes	No
5. Do supervisory personnel review the data and QC results?		
6. Does the laboratory QA Director check 5% of all projects generated?		

Comments:

IV. Quality Control/Quality Assurance - General

	Yes	No
1. Can the Quality Assurance Officer document the analysis of blind laboratory QA or PE samples?		
2. Does the laboratory maintain a project specific Quality Control Manual?		
3. Are outdated portions of the QC Manual properly archived?		
4. Does the manual address the important elements of a QC program, including the following?		
a. Personnel?		
b. Facilities and equipment?		
c. Operation of Instruments?		
d. Documentation of procedures?		
e. Preventive Maintenance?		
f. Reliability of Data?		

	Yes	No
g. Data Validation?		
h. Feedback and corrective action?		
i. QA/QC self-inspection?		

Comments:

V. Summary Checklist

	Yes	No
1. Do responses to the evaluator indicate that project and supervisory personnel are aware of QA/QC and its applications to the project?		
2. Do project and supervisory personnel place positive emphasis on QA/QC?		
3. Have responses with respect to QA/QC aspects of the project been open and direct?		
4. Has a cooperative attitude been displayed by all project and supervisory personnel?		
5. Have any QA/QC deficiencies been discussed before leaving?		
6. Have corrective actions recommended during previous evaluations been implemented? If not, provide details below.		

Comments:

E

E-2
Grain-Size (Laser Method) - SAS Request

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APPENDIX E

SAS REQUESTS

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US Environmental Protection Agency
CLP Sample Management Office
P.O. Box 818 Alexandria, VA 22313
Phone: 703-557-2490 -- FTS/557-2490

Client Request No. 1236

Special Analytical Services

Client Request

[x] **Regional Transmittal** [ ] **Telephone Request**

A. EPA Region/Client: Region II/TAMS Consultants, Inc.

B. RSCC Representative: Janet Trotter

C. Telephone Number: 908-417-1255

D. Date of Request: February 25, 1993

E. Site Name: Hudson River PCB

F. Site ID/CERCLIS ID: 84/NYD980763841

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

95 sediment samples for total organic carbon (TOC), and 19 aqueous field blanks.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analysis of approximately 95 low concentration sediment samples for total organic carbon (TOC) by Lloyd Kahn method (copy attached). Approximately 19 field blanks to be analyzed by EPA method 415.1 or 415.2.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

Superfund ARCS II RI/FS.

4. **Estimated date(s) of collection:**

May 1 through June 30 1993.

5. **Estimated date(s) and method of shipment:**

Samples will be shipped on day of collection.
Laboratory must accept Saturday delivery of samples.

6. **Number of days analysis and data required after laboratory receipt of samples:**

See Attachment A. Data reports required 35 days after laboratory receipt of samples.

7. **Analytical protocol required (attach copy of other than a protocol currently used in this program):**

Lloyd Kahn method for soil samples (see attached copy). No alternate methods will be allowed. Aqueous blanks to be analyzed by EPA MCAWW method 415.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Store samples at 4°C. Laboratory must have personnel available Saturdays (except legal holidays) to receive, log-in, and refrigerate samples.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

All documentation or legible copies shall be submitted including data sheets with data results, laboratory duplicate and method blank results, QA/QC information, standards information, raw data, calibration curves, traffic reports, sample logs, sample tracking records, and chain of custody forms. The actual method used from preparation to analysis and the date the sample was collected and analyzed must be noted. Provide a complete analysis run log showing all blanks, standards, calibrations, field samples, and all QA/QC samples associated with that batch. The report will include a written narrative describing problems encountered in receipt or during analysis and corrective actions utilized (including telephone logs, etc.). The report shall be paginated and have a table of contents. The report shall include a table cross-referencing the EPA (SAS) sample identification numbers with the laboratory's sample identification number. Laboratory calculations of standard deviation, percent recovery, and relative percent difference (as appropriate) will be provided for all QC samples.

The laboratory is explicitly required to submit documentation of its ability to perform the analysis (as specified in Section 9.1 of the L. Kahn method). This includes, but

All documentation or legible copies shall be submitted including data sheets with data results, laboratory duplicate results, QA/QC information, standards information, raw data, calculations, calibrations, traffic reports, sample logs, sample tracking records and chain of custody (COC) forms. The specific method(s) used and the date the sample was collected and analyzed, must be noted. The report will include a written narrative describing problems encountered in receipt or during analysis and corrective actions utilized (including telephone logs, etc.).

10. Other (use additional sheets or attach supplementary information, as needed):

Laboratory must provide sample calculations such that it will be clear to any independent data reviewer what was done to the sample during each step and how the final result was determined. If a computer software program is employed for calculations of merged distributions, a narrative description of it must be included.

The testing laboratory may dispose of the samples (at its own expense) after contacting Ed Garvey, TAMS, no earlier than 30 days after submission of the test report.

11. Name of sampling/shipping contact:

Edward Garvey/Esther Nelson
TAMS Consultants, Inc.
201-338-6680

12. Data Requirements

Graphical representations of the distributions are required.

Additionally, data diskette deliverables will be required for the program. Format must be Paradox, D-Base or compatible ASCII file.

Attachment A and Sections 9 and 10 of this SAS request contain further information.

13. QC Requirements:

The laboratory must analyze a sample matrix duplicate at a 5 % frequency (1 pair per 20 samples). For all fractions which represent 1% or more of the total sample, the RPD of sample matrix duplicates should be $\leq$ 20%. Field duplicates will be provided at a 5 % frequency. See Attachment A.

Deliverables as specified in Sections 9 and 10 of this SAS request.

Laboratory must submit to a pre-award audit. Audits during the program may occur at a maximum of twice monthly under the Quality Assurance Officer's direction.

14. Action Required if Limits are Exceeded:

Report all problems in narrative as described in Section 9 of this SAS request. Documentation of any actions taken to correct QC problems must be included in the data package. If sample duplicate precision exceeds criteria, reanalyze one time. Report both analyses.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

Attachment A

Analysis: Particle size distribution for 500 g and 5 g sample sizes must encompass range of 4 mm down to 0.001 mm (1 um).

Method	**QC Requirements**
ASTM D421-85 or equivalent for sieve analysis of larger particles (4mm down to approx. 1 mm)	Duplicate performed at 5% frequency Duplicate RPD criteria: < 20%
merged with:	Field Duplicates as delivered (estimate 5% frequency)
Laser Sizer Methodology (recommend Malvern 2600L) or equivalent for particle sizes down to 0.001 mm (1 um) and small sample aliquots.	

Notes:

RPD = Relative Percent Difference between a sample and sample duplicate. Calculated as:

$$\frac{\text{(Sample value(s) - Sample Duplicate value(s))}}{\frac{\text{(Sample value(s) + Sample Dup. value(s))}}{2}} \times 100\%$$

Note: RPD and duplicates refer to a single size fraction as a measure of the precision of the data for that size fraction.

For each size fraction analyzed, the duplicate frequency and RPD criteria must be met.

Attachment B

Method Summary:

Samples are well-mixed prior to analysis in order to obtain a representative sub-sample. The methodology will combine measurements made by standard sieving techniques (as referenced above) for the gravel fraction where necessary and the measurements obtained on a Malvern 2600L laser particle sizer (see manufacturer's instructions for QC and operation).

The Malvern instrument is calibrated at the factory. It employs lenses of different focal lengths to measure the concentration of particles within a maximum size range of 1800 um to 1 um. Sub-samples are introduced into the Malvern by first disaggregating in a waterbath by mechanical stirring and ultrasonic dispersion. It may be required with certain samples to perform two laser measurements: one to cover the sand fraction and the other for the silts. In these cases, the separate distributions and the sieve data are "merged" together using an algorithm to reproportion the weight percents into a single, complete distribution.

The merging algorithm must be mathematically correct; there must be appropriate overlap in the tails of the different distributions in order for the merging to be consistent. This approach, or an equivalent, should be employed to give the required complete distribution from gravel (4mm) to clay (0.001 mm) particles. For the smaller size particles, 0.120 mm to 0.001 mm, 16 sizes fractions must be defined.

E-1
Total Organic Carbon in Sediment (Lloyd Kahn Method) - SAS Request

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US Environmental Protection Agency
CLP Sample Management Office
P.O. Box 818 Alexandria, VA 22313
Phone 703-557-2490 -- FTS/557-2490

CLIENT REQUEST NO. 1237

Special Analytical Services

Client Request

X **Regional Transmittal** **__ Telephone Request**

A. **EPA Region/Client:** Region II/TAMS Consultants, Inc.

B. **RSCC Representative:** Janet Trotter

C. **Telephone Number:** 908-417-1255

D. **Date of Request:** February 25, 1993

E. **Site Name:** Hudson River PCB, N.Y.

F. **Site ID/CERCLIS ID:** 84/NYD980763841

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analysis of soil/sediment samples for grain size distribution on large (500 g) sample sizes. Complete distributions must be obtained from gravel (4 mm) down to clay (0.001 mm or 1 um) for 500g samples.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Approximately 100 soil/sediment samples for grain size (particle size) distribution analysis on 500 gm sample sizes.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

Superfund ARCS II RI/FS.

4. **Estimated date(s) of collection:**

May 1 through August, 1993.

5. **Estimated date(s) and method of shipment:**

Samples will be shipped in a single shipment following completion of each of the two phases of the project. It is estimated that about 25% of the samples will be shipped about (/ /93) and 75% of the samples will be shipped about (/ /93).

6. **Number of days analysis and data required after laboratory receipt of samples:**

Data reports required 35 days after sample receipt by laboratory.

7. **Analytical protocol required (attach copy of other than a protocol currently used in this program):**

A sieving method (ASTM D421-85 or equivalent) for the gravel fraction may be used down to 1 mm. Laser methodology (Malvern Laser Sizer) or equivalent should be used for the smaller particles between 0.001 and 1.00 mm. Separate distributions must be merged. See Attachments A and B.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc. as applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.)**

Samples must be homogenized by stirring prior to aliquoting for analysis. Particle size distribution quantitation must report down to 0.001 mm (1 um) size particles. The method specified in Attachment A is a Laser Sizer method which can handle small sample sizes and develop a distribution down to 1 um. For the 0.120 mm to 0.001 mm distribution, 16 size fractions must be reported. Alternate methodologies will be acceptable if they meet the technical requirements of this SAS request.

If more than one technique is required for different portions of the distribution, the methods must be mutually compatible (i.e., must measure the same sedimentological property). Additionally, if a single sample does require more than one technique to encompass the full size range, the separate distributions must be merged to form one complete distribution. To be mathematically acceptable there must be an appropriate overlap in the tails of the different distributions.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

is not limited to: raw data for each of the 15 replicates minimum requirement; sample weight; percent solids; instrument response; and calculated concentration; as well as laboratory calculation of the mean, standard deviation, control limits (± three standard deviations), and the control chart. The standard deviation of the 15 replicates must be less than 8.33%. The laboratory must also provide calculations of the mean and standard deviation of quadruplicate analysis performed during the analysis of the environmental samples.

10. Other (use additional sheets or attach supplementary information, as needed):

Laboratory must provide sample calculations so that it will be clear to any independent data reviewer what was done to the sample during each step and how the final result was determined.

Analysis of a mid-range calibration verification standards (check standard) is required, which must be analyzed after the initial calibration and after every 20 samples. The percent recovery criterion for the mid-range standard is ±20%.

11. Name of sampling/shipping contact:

Esther Nelson/Allen Burton
201-338-6680

12. Data Requirements

See Attachment A and Section 9 of this SAS request.

13. QC Requirements

See Attachment B and Sections 9, 10, and 14 of this SAS request.

14. Action Required if Limits are Exceeded:

The laboratory may not analyze samples until it has demonstrated acceptable performance of 15 replicates and achieved a standard deviation of 8.33% or better (so that 3SD ≤ 25%).

Duplicate, spike, and spike duplicate analysis exceeding limits will be re-spiked (as applicable) and reanalyzed once. Report both analyses. All positive detections must be associated with an acceptable calibration (including check standards and continuing calibrations, as applicable). All positive detections must be associated with an acceptable method/preparation blank, or sample concentration (prior to correction for dilution) must be at least ten times the blank concentration. All affected samples must be re-analyzed if these conditions are not met.

Sample concentrations at or exceeding the highest calibration standard will be reanalyzed using a smaller sample or diluted. Alternatively, a new calibration curve

may be prepared encompassing a higher concentration range if the laboratory can demonstrate that the calibration curve is linear throughout the expanded range.

If quadruplicate analysis RSD is not within control limits, the problem should be identified and collected, and all associated samples, including the quadruplicate, must be reanalyzed.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

Attachment A

Analysis	Method	Detection Limit	Precision	Holding Time[1]
TOC-sediment	L Kahn (2)	100 mg/kg	±3SD	13 days
TOC-aqueous	EPA 415 (3)	1 mg/l	±25%	13 days

TOC = Total Organic Carbon

Notes:

(1) Holding time begins at the verified time of sample receipt.

(2) Kahn, L., USEPA Region II, July 1988, copy attached.

(3) Method 415.1 or 415.2, Methods for the Chemical Analysis of Water and Wastes, USEPA-600/4-79-020, revised 1983.

Attachment B

Analysis	QC Audits	Frequency of Audits	Limits (% or concentration)
TOC	Calibration	1/batch (A)	±10%, or $r \geq 0.995$
	Quadruplicate	1/20 (B)	± 3SD
	Method blank	1/20 (C)	< method detection limit
	Check Standard	1/20 (D)	± 3SD

Notes:

(A) The initial calibration curve will be prepared by plotting mg carbon vs. instrument response, using four standards and a blank. Sample concentrations may not be calculated from plateaus or non-linear portions of the curve. Only a first order regression may be used for calibration.

(B) Run sample in quadruplicate every 20 samples. Report both the average and the relative standard deviation for the sample.

(C) One method blank shall be run daily per batch or one per 20 samples, whichever is more frequent. The method blank is to be brought through the entire preparation and analytical procedure, including all reagents and the same analyte-free water used for sample preparation.

(D) Verify calibration with independently prepared check standard every 20 samples. Use potassium hydrogen phthalate to prepare a 5 mg/l check standard.

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