70009

PHASE 2B
SAMPLING AND ANALYSIS/QUALITY ASSURANCE PROJECT PLAN

VOLUME 3: ANALYSIS OF ARCHIVED HUDSON RIVER SAMPLES

HUDSON RIVER PCB REASSESSMENT RI/FS

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Prepared by

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Hudson River PCB Reassessment
RI/FS Phase 2B SAP/QAPjP - Volume 3
Analysis of Archived Hudson River Samples
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* These appendices have been previously submitted to USEPA for review (Phase 2A, Volume 2 SAP/QAPjP, Revision 0, dated February 18, 1993) and are therefore not included here.
** The current version of these appendices have been submitted with the Final Phase 2A Volume 4 SAP/QAPjP (May 17, 1994) and are therefore not included here.

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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 confirmatory/geophysical 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; low-resolution coring of Upper Hudson River sediments; analysis of archived Hudson River water column and sediment samples on a PCB congener-specific basis; sediment critical shear stress analysis; and ecological sampling. Only the analysis of archived water column and sediment samples on a PCB congener-specific basis is described in this report: **Volume 3 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 Project Background

3.1.1 Site Description

The Hudson River PCB Superfund site encompasses the Hudson River from Hudson Falls (River Mile [RM] 198) to the Battery in New York Harbor (RM 0), a stretch of nearly 200 river miles. Because of their different physical and hydrologic regimes, the Upper Hudson 40 mile stretch, from Hudson Falls to Federal Dam (RM 155), is distinguished from the Lower Hudson stretch, from Federal Dam to the Battery. The part of the Upper Hudson from Bakers Falls to the Sherman Island Dam is not part of the Hudson River PCB Superfund site, but serves as a background or control area. At this time, potential remedies for PCBs in sediments at the site are limited to river bottom sediments of the Upper Hudson. However, investigations into PCBs in the Lower Hudson are an integral component of understanding the past and present migration of PCBs, dissolved or bound to suspended matter in water, from the Upper Hudson to the Lower Hudson.

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 (Sofaer, 1976; Limburg, 1984; Sanders, 1989). Discharges resulted from washing PCB-containing capacitors (untreated washings are believed to have been discharged directly to the Hudson from about 1951 through 1973 [Brown et al., 1984]) and minor spills. No records exist on which to base estimates of discharges from the beginning of PCB capacitor manufacturing operations in 1946 to 1956; however, discharges in this period are believed to be smaller. Discharges during this period have been estimated at about 30 pounds per day or 5 metric tons (about 11,000 pounds) per year (Bopp, 1979; citing 1976 litigation; Limburg, 1986; citing Sofaer, 1976). Manufacturing ceased in 1975; only minor discharges (about 0.5 kg/day or less [Brown et al., 1984; Bopp, 1979]) are believed to have occurred during facility shutdown and cleanup operations through mid-1977, when active discharges ceased, although GE had been granted a NPDES permit allowing up to 30 lbs/day to be discharged during this period (Sanders, 1989). At least 80% of the total PCBs discharged are believed to have been Aroclor 1242, with lesser amounts of Aroclors 1254, 1221, and 1016. However, the Aroclors discharged varied over time, with Aroclor 1254 being 75% or more of the total until about 1955; Aroclor 1242 being at least 95% of the discharges from about 1955 through 1971; and Aroclor 1016 being close to 100% of the discharge from 1971 through 1977 (Brown et al., 1984).

The PCBs discharged to the river tended to adhere to sediments and subsequently accumulated downstream with the sediments as they settled in the impounded pool behind the former Fort Edward Dam (RM 194.8). Because of its deteriorating condition, the dam was removed in 1973. During subsequent spring floods, PCB-contaminated sediments were scoured and transported 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 1970s. 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 closed at the same time. Both bans remain in effect. In addition to the ban on striped bass, New York has banned the sale of several other species of Hudson River fish.

USEPA under the National Contingency Plan (NCP) and Comprehensive Environmental Response Compensation and Liability Act (CERCLA), or Superfund, performed a Feasibility Study in 1984 (NUS, 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, the remedial efforts planned for the remnant deposits have been completed. The Waterford Treatment Plant treatability study concluded that the water supplied for drinking water meets Federal and State 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 (Interim Characterization and Evaluation-Review Copy) (TAMS, 1991) 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. The Phase 2A SAP/QAPjP, Revision 2 (TAMS, May 29, 1992) details the sampling tasks for Phase 2A. The complete Phase 2 Work Plan, which outlines the Phase 2A and Phase 2B investigations, was issued in September, 1992. This Phase 2B (Volume 3) SAP/QAPjP covers the third of five site investigation tasks to be conducted under Phase 2B.

3.2 Background for Archived Hudson River Sample Program

The Phase 2B analytical program for the Hudson River is separated into five basic studies as listed above in Section 3. Each study is designed to meet a specific project objective. This volume (Volume 3) of the Phase

2B SAP/QAPjP details the analysis of archived Hudson River water column and sediment samples. The archived samples represent a unique data source to the project. The samples have been collected over the last 16 years and will provide a means to directly compare the measurements of current conditions with those of the past.

The archived Hudson River samples were collected by the scientists of the Lamont-Doherty Geological Observatory (now called the Lamont-Doherty Earth Observatory or LDEO) of Columbia University between 1977 and 1991. In the process of collection and analysis, the samples were also preserved for long term storage and are available to this investigation. The samples collected by LDEO consist of two main types: water column samples; and high resolution sediment core samples. Details of the sample collection procedures are provided in Section 6.

3.2.1 Archived Water Column Samples

Large volume water column samples (nominally 10 or 20 liters) were collected into pre-cleaned bottles. For the samples collected in 1979 through 1986, the water column samples were separated by filtration into dissolved and suspended matter fractions in the laboratory in a manner similar to the current water column sampling programs being conducted for this RI. Beginning in 1983, samples were also collected as suspended particulates using an in situ (submerged) large volume filtration system (LVFS); in some cases the LVFS sample coincided with a large volume water column sample. The sample fractions were subsequently analyzed for PCBs using a packed column gas chromatograph with an electron capture detector. Packed column peaks were quantitated based on the corresponding peaks in Aroclor standards as described by Bopp (Bopp, 1979; Bopp et al., 1981). Each peak consists a mix or a group of congeners, usually of the same degree of chlorination (homologs), although in some cases a peak may consist of a pair of adjacent homologs (e.g., tricholorobiphenyls and tetrachlorobiphenyls). A suspended matter/water partition coefficient has been calculated for each of the peaks in the Aroclor 1242 standard (peaks 2 through 15) (Bopp, Simpson, and Deck, 1985; Warren et al., 1987). For each of these samples, the remaining extract was sealed in a glass vial and stored.

For samples collected in 1979 through 1981, water and particulate archived samples exist only as extracts. With one exception (Hyde Park - RM 82 - collected in September 1980), these samples exist as paired extracts. However, in some cases beginning in 1983, only particulate (filter) samples were collected. For these samples, an unextracted suspended matter sample as well as the extract still exist. No corresponding water sample or extract exists for these samples; water data were estimated using the partition coefficients calculated by Bopp et al. (1985). The suspended matter samples were originally collected onto 10 inch diameter quartz or, in some cases, glass fiber

filters which were subsequently dried and stored in sealed metal cans. The extracts and archived suspended matter samples will be analyzed by packed column gas chromatography, and the chromatograms will be compared to the original chromatograms to verify that the archiving and storage process has not altered the chemical composition of the samples or extracts. Criteria for this verification are discussed in Section 5. The archived water column samples (extracts and unextracted suspended matter, where available) which meet the criteria will then be analyzed on a PCB congener-specific basis so that these historic samples may be directly compared with corresponding data on current conditions.

The archived water column samples (dissolved phase and suspended matter) proposed for reanalysis are shown on Table 3-1. The locations at which these samples were collected are shown on Figures 3-1 (Upper Hudson) and 3-2 (Lower Hudson).

3.2.2 Archived Sediment Samples

Archived high resolution sediment core samples are available which were collected in a similar manner to the current high resolution sampling program. Most of the samples were then dried in a controlled (PCB-free) environment at 30° to 35°C (although a few of the early [1979] samples were air-dried) and stored in sealed PVC-lined aluminum cans for subsequent analysis. The core intervals were then analyzed for radionuclides by gamma counting to establish the approximate year of deposition. The dried sediment samples were subsequently extracted and analyzed for PCBs via packed column gas chromatography. Both the remaining portions of the dried samples and the sample extracts are available from LDEO for the purposes of reanalysis. The archived extracts or sediment samples will be analyzed by packed column gas chromatography, and the chromatograms will be compared to the original chromatograms to verify that the archiving and storage process has not altered the chemical composition of the samples or extracts. Criteria for this verification are discussed in Section 5. The archived sediment samples (extracts and unextracted sediment) which meet the criteria will then be reanalyzed on a PCB congener-specific basis. These samples will be compared with current core samples analyzed on the same basis to examine in situ dechlorination and degradation rates over extended periods (6 to 15 years).

The archived sediment core samples proposed for reanalysis were collected in 1977, 1983, and 1986, and are shown on Table 3-2. The locations from which these samples were collected are shown on Figures 3-1 (Upper Hudson) and 3-2 (Lower Hudson).

3.3 Project Objectives and Technical Approach

This program has two main objectives, one for each of the historic sample matrices. For the archived water column samples, the objective of this program is to obtain a data set which contains congener-specific (or at least homolog-specific) data on historic water column conditions. The use of these data is discussed in Section 3.3.1. For the archived sediment samples, the objective of this program is to obtain a data set which contains congener-specific data on historic sediment conditions. The use of these data is discussed in Section 3.3.2.

3.3.1 Objectives and Goals of the Archived Water Sample Analysis Program

The primary goal of the archived water sample analytical program described in this SAP/QAPjP is to obtain a database which will permit the study of the long-term trends in water column PCB congener concentrations and in the sources of the PCBs. Prior to 1991, nearly all Hudson River water column PCB analyses were performed on a packed column and reported on an Aroclor or peak basis. The congener specific analyses proposed in this program would more accurately define the nature of the contamination sources to the river (e.g., current spills, resuspended sediment, sewage outflows, etc.). Congener-specific data can be used to distinguish various PCB sources by using the congener mixture as a kind of "fingerprint" for the source. Information concerning the historic water column PCB congener mixture is needed in order to evaluate the long term applicability of the data obtained in the current water column analysis program.

The current water column sampling program is limited in the range of time and river conditions it can examine. It can only discern current sources which are important at the time of sampling. As was previously discussed in the Phase 1 report, the two most significant current sources of PCBs to the water column in the Upper Hudson are the Thompson Island Pool and the area upstream of Rogers Island (TAMS, 1991). Historically (i.e., since 1977), the Thompson Island Pool has contributed the largest part of the PCB load to the Hudson River (TAMS, 1991). However, recent trends in the data suggest that the contribution of the Thompson Island Pool has decreased steadily, while the contribution at Rogers Island has remained relatively constant, so that currently the contribution upstream of Rogers Island is approximately equal to that of the Thompson Island Pool. In addition, recent transient spikes (anomalous high levels of PCBs) detected in the water column (in September 1991 and June through October, 1992) suggest that a third source, possibly the abandoned mill at Bakers Falls, may exist (GE Remnant Deposit Monitoring Program, January, 1993). The results of the archived water column samples combined with the current high resolution coring program should provide a basis to evaluate the relative contributions of these

sources over the last 5 to 10 years. Both records provide a resource of water column conditions. During high flow, the suspended matter contains the majority of the PCB contamination; the high resolution coring program provides a long term average (approximately two years) of the water column conditions (i.e., the PCB concentration in the suspended matter of the water column). The water column transects represent the water column conditions at a specific instant of time. The selection of remedial alternatives for these sources can then be evaluated based on the contamination's anticipated long term importance. Data on the long term conditions should yield greater confidence in the choice and ultimate outcome of the remedial actions.

The selection of archived water column samples is limited by the available set of samples. Water column extracts or unanalyzed suspended matter samples (particulate filters) exist only for 1979, 1980, 1981, 1983, 1985, and 1986, and except for the transect sampling in 1985, no more than six locations were sampled in any year. The integrity of the archived extracts will be demonstrated by reproducing the original packed column PCB analysis of the sample extract on a gas chromatograph configured similarly to the original analytical instrument. Upon successfully reproducing the packed column results (the determination of the reproducibility is discussed further in Section 5), the sample will then be analyzed on a congener-specific basis using the GC/ECD analytical method previously developed and utilized for this project. Samples for which reproducibility of the original analysis is not obtained will not be analyzed for PCB congeners.

The selection of archived water samples focusses on the Hudson River north of the salt front (RM 58 and north). One Hudson station south of the salt front (Alpine, RM 18) has also been included for comparison of congener compositions between the Upper and Lower rivers. In addition, a set of 16 water column samples from a transect collected in October and November 1985 has also been included. This transect includes Upper Hudson and Lower Hudson stations, and stretches from RM 165.2 (Mechanicville) to RM -6 (Verrazano Narrows).

3.3.2 Objectives and Goals of the Archived Sediment Sample Analysis Program

The goal of the archived sediment sample program is to obtain a database which will permit the evaluation of in situ degradation and dechlorination of PCBs in sediment over an extended period. Degradation is defined as alterations to a PCB molecule from which the resulting product(s) is no longer a PCB. Degradation is differentiated from dechlorination, in which a PCB molecule (e.g., a tetrachlorobiphenyl) loses a chlorine atom (or atoms), but the resulting molecule is a lesser chlorinated, lower molecular weight PCB (e.g, a trichlorobiphenyl). The rates for degradation and dechlorination of PCBs within the sediments of the Hudson is currently poorly defined. Current

studies available on biodegradation and dechlorination of PCBs are primarily limited to laboratory studies where the rate of degradation is measured for relatively short periods of time under highly controlled conditions. The occurrence of degradation and dechlorination would increase the percentage of mono- and di-chlorobiphenyls relative to the more chlorinated biphenyls. The archived sediment analysis program will directly examine the in situ rates of degradation and dechlorination by comparing dated sediment core layers from the current high resolution sediment cores and the corresponding archived high resolution sediment cores. Dechlorination can be determined by the presence of specific indicator congeners which were not part of the original mixture (or present at a much smaller fraction) and are known as dechlorination products (Rhee et al., 1993a; Rhee et al., 1993b). Changes in the ratios of homologs (e.g., trichlorobiphenyls to monochlorobiphenyls) relative to the original homolog mixtures can be another indication of dechlorination.

This program will consist of comparing sediment core layers from a given location with matching dates of deposition (e.g., the 1963 layer in the archived core from River Mile 188.6 (RM 188.6) with the 1963 layer in the current RM 188.6 core) and examining the differences in PCB congener concentrations and congener ratios between the two layers. Differences between the reanalysis of the archived extracts or samples and those collected and analyzed as part of this RI/FS which can be attributed to biological or in situ activities will be used to estimate the rate of in situ dechlorination or degradation. The archived high resolution sediment core samples will be analyzed on a congener-specific basis so that the results are directly comparable to those obtained for the corresponding current high resolution core samples.

The basic premise of this approach rests on the integrity of the archived samples (i.e., no changes occurred in the archived sediment sample as a result of the archiving process or long term storage). Review of the procedures used for archiving the samples suggests that the PCB concentrations should not be affected by the archiving and storage process, and a limited study by Bopp indicated that archived sample reproducibility was good over about a 15 month period (Bopp, 1979). This archive sample analysis program will include a more rigorous verification of archived sample integrity. Initially, this will be evaluated by analysis of nine samples (plus two duplicates) collected during the high resolution coring effort in 1992 and subsequently archived by a method similar to that used for the historical archived samples. If the data from the 1992 archived samples is comparable to the data obtained from the same samples prior to archiving (i.e., there are no apparent effects on the data resulting from archiving and storage), then this program will proceed to the next step. A statistical test(s) will be used to compare the two data sets (i.e., the wet sediment data, and the corresponding analyses of the 1992 archived samples).

Assuming there is no statistically significant difference between the data sets, the next step will be the packed column GC reanalysis of the archived samples and subsequent comparison to the original chromatograms.

The approach of comparing archived to current high resolution core analyses also assumes that little core-to-core differences exist as a result of spatial heterogeneity. High resolution cores are defined by their reproduction of the known Cesium-137 (Cs-137) depositional history for the New York State region. The current high resolution coring sites were selected based on successful previous coring efforts at these locations. Because of the similarities in the Cs-137 and PCB release histories to the Hudson watershed (Olsen, 1979; Bopp, 1979), sediment layers of comparable age with similar Cs-137 levels also have similar PCB concentrations (Bopp, 1979; Bopp and Simpson, 1989). In the current high resolution coring program, lower Hudson core tops (i.e., the 1991 to 1992 sediment layer) varied by less than one order of magnitude - from about 0.5 ppm to 3.0 ppm total PCBs - over a 145 mile stretch of river. Data from the high resolution coring program also demonstrate low variation of total PCB concentrations (approximately 20%) between cores which are located 20 miles apart in the lower river, indicating little core-to-core spatial heterogeneity (see also Bopp and Simpson, 1989).

Based on these assumptions, differences between archived and current sediment core layers are the result of in situ processes which have transformed the sediment layer PCB concentrations or PCB congener distributions from those measured at the time of the collection of the archived core to those at the time of collection of the current core. If degradation has occurred, the total PCB concentration would be lower in the equivalent layers of the new core. However, dechlorination would be observed by a shift in the PCB congener distribution, to the lower molecular weight congeners (i.e., those with fewer chlorines) and not necessarily a major change in total PCB concentration. Since PCB data are reported on a weight basis (mass of PCBs per mass of sediment), loss of a chlorine atom does reduce the reported concentration of PCBs; however, dechlorination would radically change the congener-to-congener ratios of the original PCB mixture. These dechlorination patterns have been previously studied in laboratory settings (Rhee et al., 1993; Brown et al., 1993). Since the time of collection is known for both cores, the changes noted can then be used to calculate a rate of transformation. In addition, by examining the older core layers (e.g., 1954 and 1963) and comparing them with the more recent core layers (e.g., 1974 and 1977), it should also be possible to examine the effect of sediment age on the rate of transformation.

The analysis of current and archived high resolution core layer pairs by itself will not absolutely determine the rate of in situ transformation but will be used in conjunction with other available literature to resolve this issue for the purposes of the Reassessment. The importance of this information to the Reassessment cannot be

overemphasized. Estimates between 51,000 lbs and 133,700 pounds of PCBs are believed to be sequestered in the sediments of the Thompson Island Pool alone (M.P. Brown et al., 1988b; Malcolm Pirnie, 1978). Another 187,000 pounds (85,000 kg) are believed buried in the sediments of the Lower Hudson (Bopp and Simpson, 1989). Understanding the long term fate of these PCBs in the Hudson has important implications for the selection of an effective remedial approach since it is likely that these sediments will play a significant role in governing water column and fish PCB levels for the foreseeable future.

3.4 Sample Locations

The sample locations are obviously limited by the availability of historic samples. The proposed archived water column samples were collected at the locations shown in Figures 3-1 and 3-2. The majority of these locations consist of suspended matter/dissolved phase pairs which have been extracted and exist only as hexane extracts. Also shown are the locations of very large volume suspended matter samples. Some of these suspended matter samples were never analyzed for PCBs and exist as the original archived, dried suspended matter on quartz or glass fiber filters.

The archived sediment samples were collected at many of the current high resolution sediment core locations. The archived sediment core samples to be analyzed for this program are shown in Figures 3-1 and 3-2.

3.5 Sample Analyses

Because of the irreplaceable nature of the samples, it is planned that samples will be hand delivered to the analytical laboratory by the TAMS sample manager or designee. Samples will be shipped by commercial delivery service only if hand delivery of some or all samples proves impractical. The analysis at the laboratory will be subject to oversight by TAMS or other project personnel as well. Samples will be delivered in one of three forms; i.e., as a hexane extract, as dried sediment, or dried suspended matter (unanalyzed filters), although hexane extracts will be used predominantly. Dissolved phase water samples will be delivered as hexane extracts, representing the original sample preparation. In these cases, none of the original material exists since it was entirely consumed in the preparation of the extract. A limited number of suspended matter samples which exist only as dried suspended matter on filters may also be included for analysis. These samples were never analyzed for PCBs, and thus no extract was ever prepared for these samples.

A summary of the approach to the PCB congener analytical program for the archived samples is presented below. More details on various aspects of this program are provided in Sections 5 and 6 and the Appendices.

3.5.1 Archived Sediment Sample Analysis

Archived sediment samples will be delivered as hexane extracts to the laboratory. The archived sediment sample will only be used in situations in which an important PCB extract is missing or inadequate (e.g., the extract has evaporated, or there is other evidence of extract integrity not being maintained). The extraction procedure used to generate the archived PCB fraction hexane extracts did not completely extract the monochlorobiphenyls and possibly to a lesser extent some of the dichlorobiphenyls. However, the second archived extract fraction (originally extracted with methylene chloride but then solvent exchanged to hexane), containing the remaining mono- and di-chlorobiphenyls, originally to be used for pesticide analysis, also exists for these samples, and this archived pesticide extract will also be analyzed for PCB congeners. The results from the analysis of the two extracts will be mathematically combined to report all the PCB congeners. As a part of the MDL development for the current high resolution sediment coring program, the original sediment preparation procedure used by Bopp (Bopp, 1979) in the preparation of the hexane extracts was duplicated and found to incompletely recover the monochlorobiphenyl congeners (approximately 75% were recovered by mass). Changes in the monochlorobiphenyl levels are expected to be important indications of the occurrence of in situ degradation and thus must be accurately determined in both the current and archived sediment samples.

In cases where the archived dried sediment, and not the hexane extract, will be analyzed, it is necessary to demonstrate the integrity of the archived sediment sample relative to the original analysis. For this reason, two extracts will be obtained from separate portions of each archived sediment sample. One extract will be obtained by replicating the original extraction procedure used by Bopp (Appendix A-10). This extract will be analyzed by packed column gas chromatography (Appendix A-11) so that the results can be directly compared with the original analysis by Bopp so as to evaluate sample integrity. The second extract will be obtained by the current extraction procedure (Appendix A-3) followed by capillary column gas chromatography (Appendix A-4) so that these results can be directly compared with the current high resolution sediment core sample results.

3.5.2 Archived Water Sample Analysis

The extraction procedure used by Bopp which split the monochlorobiphenyl congeners between the hexane and methylene chloride extracts in sediment samples also affects the hexane extracts prepared from the water samples. In addition, as noted above, the original water samples were completely consumed in extract preparation and are not available for re-extraction. The end result is that each water sample exists as two extracts which can potentially be used to quantify historic water column concentrations of PCBs congeners. The split extraction procedure used by Bopp resulted in the monochlorobiphenyls being split between the PCB (hexane) extract and the pesticide fraction extract, with the extractable balance of the monochlorobiphenyls (i.e., those not in the PCB portion of the extract) remaining in the pesticide portion of the extract. Both extracts will be analyzed for each water sample in this program. In the absence of any other historic data at the congener level, the archive water sample results for the monochlorobiphenyls, derived from the mathematical combination of the results from both extracts, should still be usefui to the project. Reanalysis of both portions of the extracts is necessary to obtain full recovery of the monochlorobiphenyls.

3.6 Schedule

The archived sample analytical program includes two parts - archived water samples, and archived sediment samples. In each case, the program consists of several tasks, including archived sample selection, packed column GC analysis, evaluation of the packed column data and comparison to the historical data and chromatograms, capillary column (congener-specific) analysis, and GC/ITD congener confirmation.

3.6.1 Archived Water Sample Analysis Schedule

The archived water sample analysis program is scheduled for the summer of 1993. Sample extracts will undergo two analyses as part of this program: PCB analysis by packed column gas chromatography; and congener-specific PCB analysis by capillary column gas chromatography. The packed column analysis is intended to verify the integrity of the sample extract. To accomplish this, the results of the packed column analysis will be compared with the historic packed column analytical results. The analytical data will be evaluated for packed column peak resolution, peak quantitation and relative peak ratios. The criteria for these characteristics are presented in Section 5. Those samples satisfying these criteria will then be sent for congener-specific analysis.

PCB congener confirmation analyses (by GC/ITD) will be conducted on about 5% of the hexane extracts of water samples analyzed for PCB congeners.

3.6.2 Archived Sediment Sample Analysis Schedule

The archived sediment sample analysis is scheduled for the summer of 1993. However, the analysis of samples from any historic high resolution core is contingent upon the completion of two tasks underway as part of the current high resolution coring program. The first task involves the completion of the analysis of the current high resolution core for PCBs (congener basis) and radionuclides. The second task involves an evaluation of the drying procedure used for sediment storage. These data are needed to verify that the current effort was successful in obtaining an interpretable, dated core with reliable PCB data. The historic sediment core samples cannot be evaluated for the purposes of this program without a matching current core.

Once the results from these tasks are obtained and reviewed, the archived sediment extracts (PCB fraction only) or samples from the archived core will be analyzed for PCB Aroclors by packed column GC. It is anticipated that 4 to 5 archived sediment core samples will be analyzed for each high resolution coring location. These samples will correspond to temporally well-matched layers based on the radionuclide chronologies for the core pairs. The packed column Aroclor data will be compared to the historic data and chromatograms. As was the case with the water samples, only those samples meeting the comparability criteria will be subject to capillary column PCB congener analysis. Both the PCB and pesticide extracts of the original samples will be analyzed for PCB congeners.

PCB congener confirmation analyses (by GC/ITD) will be conducted on about 10% of the sediment sample extracts analyzed for PCB congeners.

Table 3-1
Archived Water Column Samples to be Analyzed

Station	River Mile*	No. Of Samples	1979				1980				1981				1983				1984		1985		1986	
			W	M	S	M	W	M	S	M	W	M	S	M	W	M	S	M	S	M	S	M	S	M
Fort Miller	186.1	1															ext., part.	7						
Schuylerville	181	4													ext.	3,4	ext., part.	3,4						
Merchanicville	165.2	6													ext.	3,4	ext., part.	3,4,7			ext., part.	11		
Waterford	156.6	1																	ext., part.	6				
Mohawk at Rexford	NA	5															ext., part.	3,4,7	ext., part.	6	ext., part.	11		
Troy	152.7	7													ext.	3	ext., part.	3,4,7	ext., part.	6	ext., part.	11	ext., part.	4
Albany	145	4	ext.	10,11	ext.	10,11																		
Alsen	110	1																					ext., part.	4
Wanton Island	107	1																			ext., part.	11		
Kingston	90	2	ext.	10	ext.	10																		
Hyde Park	82	1					ext.	9	ext.	9														
Highland	77	2																			ext., part.	11	ext., part.	4
Cornwall	58	5	ext.	10	ext.	10	ext.	9	ext.	9											ext., part.	11		
Stony Point - deep	40	1																			ext., part.	11		
Stony Point - surface	40	1																			ext., part.	11		
Tappan Zee - surface	27	1																			**	11		
Tappan Zee - deep	27	1																			**	11		
Alpine - surface	18	8	ext.	8	ext.	8	ext.	9	ext.	9	ext.	6	ext.	6					ext., part.	6	ext., part.	10		
Alpine - bottom	18	1																			ext., part.	10		
Upper Harbor - Bottom	6.5	1																			ext., part.	10		
Upper Harbor - surface	6.5	1																			ext., part.	10		
Verrazano Narrows - surface	-6	1																			ext., part.	10		
Verrazano Narrows - bottom	-6	1																			ext., part.	10		
Totals		57																						

NOTE: * = River Mile Point is approximated within +/- a half mile

** = Sample may be available

W = Water sample; S = Suspended matter sample; M = Month; ext. = Extract; part. = Unanalyzed filter with suspended matter (particulates).

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Table 3-2

Archived Sediment Core Samples to Be Analyzed

Archived Core Sample				Current High Resolution Core Sample	
RM	Location	Collection Date	Number of Samples	Core Number	Core Location
191.1		1983	4	20	191.2
189.2	Thompson Island Pool	1983	4 or 5	23	189.2
188.5	Rogers Island	1983	4 or 5	19	188.6
166.3	North of Mechanicville	1983	?	16	166.2
N/A	Mohawk	1977?	3	13	Mohawk
143.4	Albany Turning Basin	1977	4	11	143.5
88.6	Kingston	1986	4 or 5	10	88.6
91.8	Kingston	1977	2 or 3	10 (Note 1)	88.6 (Note 1)
60	Dennings Point	198?	5	9	59.55
43.2	Lents Cove	1977	5	6 and 7	43.15
-1.7	(high deposition)	1977	2 or 3	2	-2.0
-1.65	(slower depostion)	1977?	2 to 5	3	-2.1

Note 1: The current High Resolution Core taken at RM 88.6 (Core #10) is considered to be comparable to the archived core collected in 1977 at RM 91.8, as well as the archived core collected at RM 88.6 in 1986.

4 Project Organization

The project team will consist of representatives from USEPA Region II, TAMS Consultants, Inc., Gradient Corporation, technical consultants, subcontractors, and analytical laboratories. A Phase 2B archived sample analysis program organization chart is provided in Figure 4-1.

The TAMS Project Manager, Albert DiBernardo, reports directly to Douglas Tomchuk, the USEPA Remedial Project Manager (RPM). TAMS will provide overall project management services for the Phase 2B activities. Gradient Corporation, subcontractors to TAMS, will provide technical consulting services for chemistry and laboratory activities. Archived samples will be provided by the staff of the Rensselaer Polytechnic Institute (RPI) Department of Earth and Environmental Science under the supervision of TAMS personnel. RPI staff will also oversee the laboratory operations as directed by TAMS personnel.

4.1 Operations Responsibility

The TAMS Project Manager (PM) will be responsible for overseeing the overall analytical program, including the final sample selection and analysis. Dr. Richard Bopp of RPI will be the Sample Manager (SM) and be responsible for providing the archived samples and delivering them to the analytical facility.

4.2 Laboratory Responsibilities

The TAMS/Gradient Quality Assurance Officer (QAO), Dr. A. Dallas Wait, will monitor the activities of the TAMS-contracted analytical laboratories. He will be responsible for overseeing the implementation of the technical and recording requirements of sample analyses in accordance with this SAP/QAPjP. Dr. Wait will be assisted in this role by Dr. Bopp of RPI.

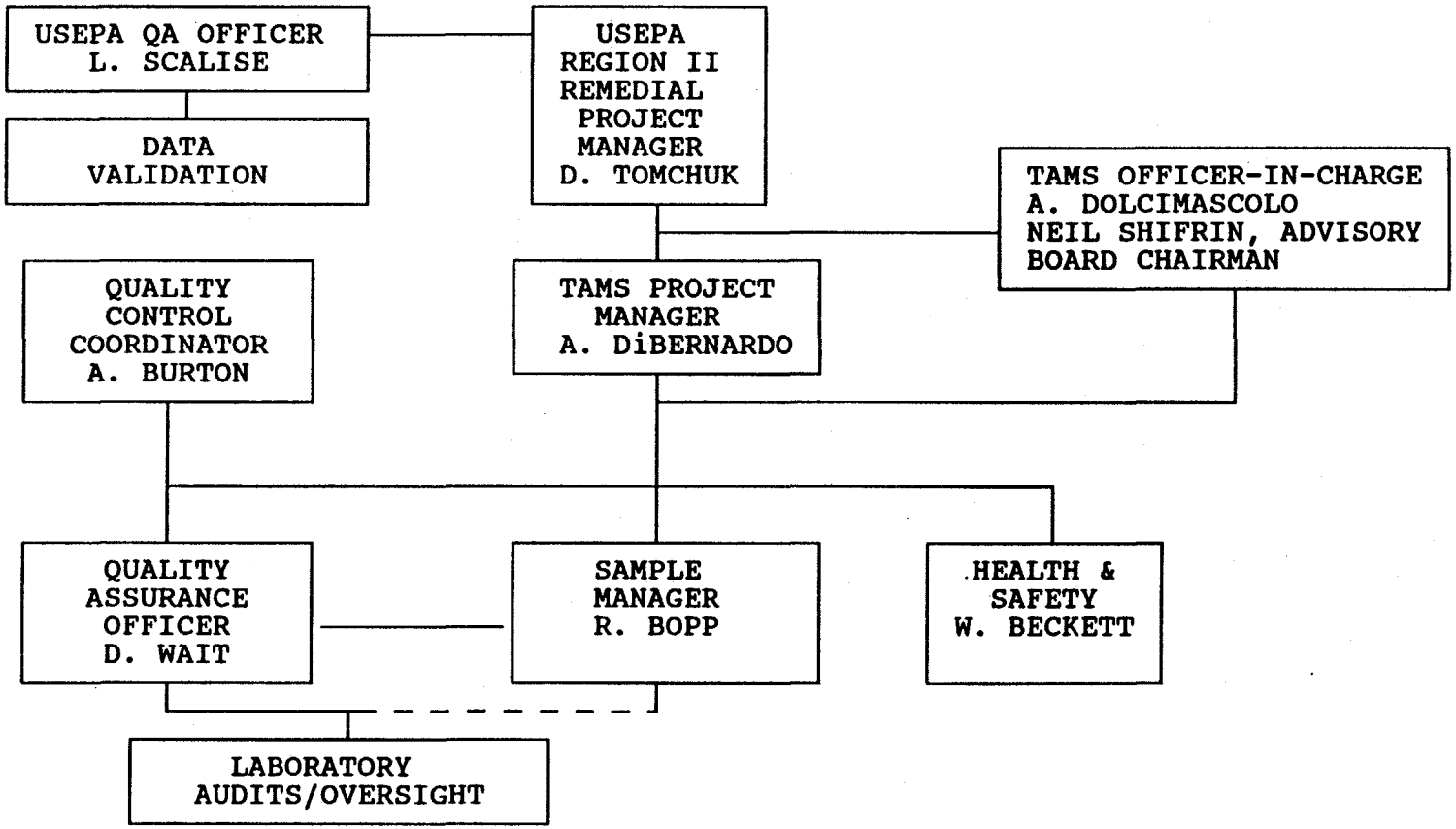
The TAMS/Gradient Quality Assurance Officer will be involved with the selection of TAMS-contracted laboratories. Selection criteria may include a pre-award audit of the laboratory. Criteria to be used in the audit evaluation will be similar to that used by EPA to audit CLP laboratories.

4.3 Quality Assurance Responsibilities

Due to the nature of the archived extracts and samples to be analyzed in this program, no formal field operations or chain-of-custody procedures were instituted prior to the initiation of this program. Formal chain-of-custody procedures will be initiated prior to delivery of the samples to the laboratory. Dr. Bopp shall be responsible for initiating a chain-of-custody for all samples to be analyzed. The TAMS/Gradient Quality Assurance Officer will oversee quality control/quality assurance issues for the laboratory. In addition, the laboratory chosen to perform the analysis will have its own QA Director to monitor internal quality control. The EPA Region II Quality Assurance Officer for this project, Laura Scalise, will be involved with the approval of this SAP/QAPjP, and then monitor its implementation.

Validation of PCB congener data will be the responsibility of USEPA. Validation will be in accordance with the protocols developed by TAMS/Gradient and approved by USEPA specifically for this project (Appendix A-6 and A-7). Evaluation of packed column PCB analyses will be the responsibility of TAMS/Gradient personnel under the direction of the project QAO or TAMS' ARCS Quality Control Coordinator, Allen Burton.

FIGURE 4-1
HUDSON RIVER REASSESSMENT RI/FS
PHASE 2B ARCHIVED SAMPLE ANALYSIS PROGRAM ORGANIZATION



5 Quality Assurance Objectives for Measurement Data

The primary objective of the Quality Assurance (QA) program is to provide data of sufficient quality and quantity to achieve the project objectives as stated in Section 3. A further discussion of the data quality necessary to achieve these objectives is presented below (Section 5.1). 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, 1987). 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 the QA objectives will be evaluated to determine the extent to which 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 Section 5.2, and procedures for monitoring these parameters are discussed in Section 5.3.

5.1 Data Quality Objectives

As discussed in Section 3.3 of this SAP/QAPjP, the primary objective of the archived sample analysis program is to obtain a data set which will permit the comparison between current and historic PCB levels on a direct basis. This requires that current and historic PCB congener concentrations and the relative congener distribution be determined by comparable analytical procedures. Where differences exist between historic sample collection procedures and those utilized for this program, it is important that these be noted and communicated to the data user so that inappropriate comparisons between dissimilar data are not made. Because of the complex distribution of PCBs in the water and sediments of the Hudson River, congener-specific PCB analysis has been or will be performed on all current river samples collected for the Phase 2 investigation. To maximize the comparability of the current and archived water column and sediment samples, the archived samples must also be analyzed on a congener-specific basis.

A viable basis for comparison also requires that the integrity of the all samples be maintained from collection to the congener-specific analysis. This is accomplished for the current sampling effort by following the guidelines for sampling handling and custody procedures and quality assurance monitoring as set forth in the various SAP/QAPjPs prepared for this investigation. For the archived samples, there was no formal SAP/QAPjP covering the sample collection or original analysis, so sample integrity must be established from the available field and laboratory records for each sample and on the reproducibility of the original analysis under the current analytical

program. To this end, the current analytical program will involve two analyses of each archived sample. The first analysis involves replicating the original analytical procedure and confirming that the sample still contains the analytes previously detected at levels comparable to those originally quantified, and that comparison of the chromatograms shows an acceptable degree of reproducibility, including early eluting peaks (e.g., monochlorobiphenyls) not quantified in the original analysis. The second analysis is the program-standard congener-specific PCB analysis.

The ability to reproduce the original analyses is clearly dependent upon the archiving and storage procedures. The procedure used to evaluate the archiving process and its potential effect on data comparability is discussed below (Section 5.2.4.2). Two forms of archived samples were generated from sediment core samples. The first process involved drying the sediment samples under controlled conditions soon after collection with subsequent archive storage in air-tight metal cans. When sediment dating (via radionuclide measurement) was completed, an aliquot of the sample was removed from the can for packed column PCB analysis, and the can was resealed. The dried sediment was then extracted and analyzed. The second form of archived sediment core sample consists of the extracts (prepared for GC analysis) produced from these samples, which were archived by storing the extract in a teflon-sealed screw-cap vial at low temperature ($< 0°C$).

Two types of archived samples are available for historic water samples - suspended matter samples (filters) or extracts, and dissolved phase PCB extracts. However, unlike the sediments, only one form generally exists for each sample. After collection, water samples were separated into "dissolved" and suspended matter fractions by filtration in a fashion essentially identical to the water sample procedures used in this investigation. All dissolved fractions and most suspended matter fractions were subsequently extracted for PCB analysis. These extracts were also prepared in a manner similar to the current procedures. However, the preparation of the water (dissolved phase) extracts required the entire sample, and therefore none of the original aqueous sample material (dissolved fraction) is available for previously analyzed water samples. However, the extracts are available, archived according to the same procedures as the sediment extracts. A small number of historic suspended matter samples are available as dried particulate matter on filters stored in air-tight metal cans. Some of these samples are from multiple filters collected in 1983 and have associated particulate extract analysis; others of these samples have never been analyzed for PCBs.

Some of the suspended matter samples planned for analysis do not have associated water sample extracts; this is the case for some archived samples collected after 1983. However, as mentioned earlier (Section 3.2.1),

suspended matter/water partition coefficients have been calculated (e.g., Bopp, Simpson, and Deck, 1985; Warren et al., 1986) and estimates of water concentrations can be made on a peak, homolog, or total PCB (aroclor) basis from the suspended matter data.

5.2 PARCC and Sensitivity Objectives

PARCC and sensitivity objectives have been developed for the archived samples and extracts based on sample objectives, analytical methods, historical data (examined in a qualitative sense) and published guidelines for the EPA Contract Laboratory Program (CLP) as listed in Section 17 (References). Specific numerical criteria for PARCC and sensitivity goals are developed for each analytical method (i.e., packed column gas chromatography and congener-specific capillary column gas chromatography) to achieve the project-specific DQOs.

PARCC objectives for Phase 2B sampling are summarized on Tables 5-1 and 5-2 for the packed column and capillary column gas chromatography analyses, respectively. Sensitivity (detection limit) objectives for each method are listed in Tables 5-3 and 5-4, respectively. Reproducibility criteria between the current and historic packed column gas chromatographic analyses are given in Table 5-5. Although all PARCC parameter and sensitivity objectives are important, comparability of data sets is the most important for the archived sample analytical program.

5.2.1 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 the average value. Precision is usually expressed in terms of relative percent difference or relative standard deviation. Measurement of precision is dependent upon sampling technique and analytical method. Historic sampling techniques will be reviewed against the current techniques to only select those samples where the techniques are as consistent as possible.

Quality control (QC) samples, including laboratory (matrix) duplicate samples, and matrix spike and matrix spike duplicate samples will be analyzed and used to measure precision. An additional measure of precision 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 matrix spike/matrix spike duplicate.

The availability of true field duplicates is limited by the available samples but will be analyzed where possible up to the frequency of one in twenty samples. For this part of the program, the three matrices are defined as: (1) hexane extracts of water, sediment and suspended matter samples; (2) dried sediment samples (if any are analyzed); and (3) dried suspended matter (archived filters). Where multiple (unanalyzed) filters exist and have been archived, separate analysis of two filters will provide field duplicate data for that matrix. For the other matrices, field duplicates do not exist; analytical (laboratory) duplicates will be used instead. Analytical duplicates will be obtained by splitting extracts, a single archived filter (suspended matter) samples or sediment samples to meet the one duplicate per 20 samples criterion. For samples analyzed only as extracts, duplicates will consist only of replicate analysis of the same extract at a one in 20 frequency. Analytical duplicate 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 USEPA Region II data validation protocols, data may be fully usable even if these objectives are not met.

5.2.2 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. Surrogate spikes, matrix spike blanks, performance evaluation (PE) samples, as well as matrix spike QC samples, will be used to measure accuracy for project samples.

It is acknowledged that there may be some loss of accuracy due to the extended storage time associated with these samples. To compensate for the long storage time, each sample will be analyzed via the original packed column analysis technique to evaluate the effects of long term storage. Only those samples that meet the identification and reproducibility criteria listed in Tables 5-1 and 5-5 will be analyzed via the congener-specific PCB method.

Method Detection Limit (MDL) studies performed for this program indicate that the extraction procedures used in the historic analysis program may not completely recover some monochlorobiphenyls. For comparison of the packed column data sets, this is not significant if the error (i.e., low recovery) is consistent within and between data sets. It is necessary, however, to know how much error is introduced from the extraction and archiving of

dried sediment samples, since some to the comparisons involve wet sediment analyses conducted on high resolution core sediment core samples collected in 1992 to reanalysis of samples dried and extracted previously. In order to determine the accuracy of the archiving and subsequent extraction procedures, a number of the high resolution core samples collected in 1992 were archived in a manner identical to that used to generate the historical archived samples. It is planned that nine of these recently archived samples (representing three concentration ranges from three different locations), plus two duplicates, will be analyzed for PCB congeners at the beginning of the archived sample analytical program. These data will be compared to the corresponding data from the wet sediment analyses already conducted. The comparative data should be adequate to quantitatively assess the effect of the archiving and storage process on the accuracy of the congener analysis; if necessary and appropriate, correction factors may be determined so that wet sediment analytical data can be compared to dried, archived sediment data, and so that the true value of the PCB congener concentrations in the archived samples can be estimated.

Improvements in the extraction procedures used for this RI/FS have resulted in increased recoveries of the mono- and di-chlorobiphenyls, relative to the recoveries in the archived samples. In order to improve the accuracy of the PCB congener analysis of the archived extracts in quantitation of the monochlorobiphenyls, both the archived PCB fraction extract and the archived pesticide fraction extract will be analyzed by capillary column GC/ECD. The Monochlorobiphenyl and dichlorobiphenyl data from the pesticide fraction extract will be added to the congener data from the PCB extract analysis. The analysis of the pesticide fraction of the archived extracts will also improve the comparability of the data sets (i.e., reanalysis of archived extracts for PCB congeners as compared to PCB congener analysis of the corresponding samples obtained during this RI/FS).

5.2.3 Representativeness

Representativeness expresses the degree to which sample data represents the characteristics of the medium or matrix from which it is collected. Samples that are considered representative are ones that are properly collected to characterize the nature and extent of contamination at a given location. Representativeness has been considered in the selection of the archived samples. The selection of these samples is based on the original historic analysis, location and time of collection so as to best represent the historic conditions. In addition, only those samples whose collection methods were consistent with the current sampling methods will be considered for analysis under this program. For large volume suspended matter samples (the only matrix for which true duplicates are available), comparison of the analytical results from field replicates will provide a direct measure of individual sample representativeness.

5.2.4 Comparability

Comparability is a qualitative parameter expressing the confidence with which data sets can be compared. General criteria for comparability are discussed below in Section 5.2.4.1. However, due to the importance of demonstrating the comparability and integrity of historical samples and analyses of archived, specific procedures and criteria have been established for this purpose for this project. These are discussed below in Section 5.2.4.2.

5.2.4.1 General Criteria for Comparability

Comparability is a function of the degree to which various measurements quantify the same unit or property (e.g., total PCBs quantified as Aroclors, as opposed to congener-specific PCBs), and the similarity of measurement methods (including sampling, extraction, and analytical methods). Comparability also relies upon precision and accuracy to be within appropriate QC limits before the data can be used for comparison of data sets. This will be accomplished through the consistent use of the analytical methods described in this SAP/QAPjP (Section 6) and by selecting current and archive sample pairs collected and prepared by the same methodology. In the case of the archived sediment samples, the pair selection will also depend upon the analysis of core radionuclide chronologies, so that each sample from a current high resolution core/archived high resolution core pair will represent the same sediment horizon. Additionally, quantitative and qualitative information on comparability will be obtained for the PCB congener analyses in 10% of the sediment and particulate (suspended matter) samples (including extracts) and 5% of the water sample extracts by GC/ITD confirmation (Appendix A-5).

For this project, internal comparability (both within and between different parts of the program) is of high importance. Specifically, the ability to draw conclusions regarding differences between current and archived samples requires that such data be reported on a consistent basis. Therefore, all archived samples to be analyzed under this program must have been collected and prepared by techniques consistent with those used for the current investigation.

Establishing the comparability or reproducibility of the historical analyses is a necessary component of demonstrating the integrity of the archived samples and extracts. Therefore, each of the PCB packed column analyses performed under this program will be compared to the original (historical) analysis of the same sample. If the reproducibility criteria are not achieved, it will be assumed that there is no defensible evidence of the sample

or extract integrity, and samples not achieving the criteria will not be subject to further analysis. A sample chromatogram of the historical analysis is shown on Figure 5-1, and the reproducibility criteria (i.e., precision and accuracy criteria for comparing the data) are shown on Tables 5-1 and 5-5.

As discussed in Section 5.2.2, there may be inherent differences in the data generated from analysis of wet sediment samples, as was performed for the current program, as compared to the analysis of extracts of dried, archived sediment samples. The analysis of archived samples generated during the current high resolution sampling program described in Section 5.2.2 is expected to provide a quantitative basis for evaluating the comparability of the two data sets.

Some water column samples collected beginning in 1983 were collected in a different manner than used for historical samples collected from 1977 through 1983 (i.e., large volume filter samples, or LVFS). The water column sampling procedure utilized for the current investigation is comparable to that used for the historical large volume (nominally 10 or 20 liter) water column samples, which were laboratory-filtered to split into dissolved phase and suspended matter (particulate phase) samples prior to extraction. Differences in data generated from the two sample collection procedures have been noted (Bopp, Simpson, and Deck, 1985). To the extent that the equilibration study conducted as part of the Phase 2A water column transect program and other research cannot account for the differences observed between the LVFS and laboratory filtration data, the comparability of data between these two sample types may be limited.

Archived samples and chromatograms appear to indicate that two different chromatographic columns (3% SE-30, and 4% SE-30/6% OV-210 on a 2 mm ID, 6 m packed glass columns) were used for the historic analyses and in the literature. Chromatography generated by these two columns is nearly identical (Richard Bopp, personal communication). This will be verified prior to the initiation of this analytical program. Therefore, only the 4% SE-30/6% 0V-210 column is specified in the packed column analytical SOP in Appendix A-11.

This investigation also includes PCB congener analysis of the archived pesticide fraction extracts, which are expected to contain up to 30% of the total recoverable monochlorobiphenyl congeners, along with a lesser percentage of the dichlorobiphenyls. However, due to the expected inability of the packed column analysis to separate or quantitate these peaks (mono- and di-chlorobiphenyls) in the pesticide extracts, no packed column analysis will be performed on the archived pesticide extracts. Packed column analysis will be restricted to the archived PCB fraction extract.

5.2.4.2 Procedures for Evaluating Comparability of Archived and Wet Sediment Samples

The ability to make valid conclusions based on comparisons of data obtained from wet sediment samples (e.g., the high resolution coring samples collected for this RI/FS in 1992) to data from the archived (dried) sediment samples collected previously is clearly dependent upon the assumption that the archiving process itself does not result in an alteration of the chemical (PCB congener) composition of the sample. In order to verify this assumption, the first step of the archived sample analysis program will be to re-analyze eleven samples (three concentration levels from each of three sample locations, plus two duplicates) which were collected during the high resolution coring program and initially analyzed as wet sediment samples. These samples were then dried and archived in a manner essentially identical to that used for generating the archived sediment samples. The data from the reanalysis of these samples as dried sediments will be compared to the data from the initial analysis as wet sediment samples. Since the purpose of this evaluation is to establish the comparability of the archiving process, statistical tests (e.g., *t*-test) will be used to evaluate the comparability of the two data sets (as opposed to a sample-by-sample evaluation). Special attention will be paid to the affect of the archiving process on the lower molecular weight congeners for two reasons: first, due to their relatively higher volatility, these congeners would be more susceptible to loss in the archiving process; and second, data for these congeners is critical in drawing conclusions regarding in situ process in the Hudson River sediments.

5.2.4.3 Specific Procedures for Assessing Comparability of Historic and Current Analytical Data

After is has been established that the archiving process does not result in alteration of the samples (discussed above in Section 5.2.4.3), it is then still necessary to establish the integrity of the individual extracts derived from these samples, or the integrity of the samples themselves. The criteria for comparing the current and historic packed column GC analyses are discussed below.

5.2.4.3.1 Total PCB Aroclor Quantitation Criteria

Quantitation of total PCBs as total PCBs or individual Aroclors based on the current analysis must agree with the historic quantitation within $\pm 50\%$ relative percent difference (RPD); quantitation must be calculated in the same way and be based on comparable Aroclor standards (see also Section 5.2.4.2.5, below). Only a very limited amount of data from the archived samples was ever quantitated as Aroclors; most samples were reported as total PCBs based on a summing of individual peaks using the procedure described in Appendix A-11.

5.2.4.3.2 (Relative) Peak Distribution (Abundance) Criteria

The ratios of all major peaks relative to the largest PCB peak in the historic chromatogram must agree to within 20% RPD. The calculation procedure for this is defined in Section 14.1.1. A major peak is defined as representing 10% or more of the sample mass (or instrument response) of the largest peak in the historic analysis.

5.2.4.3.3 Low Molecular Weight Congener Criteria

The historic analysis of the archived samples was not particularly concerned with the low molecular weight congeners (mono- and di-chlorobiphenyls). No monochlorobiphenyl peaks were considered in the historic analyses, and dichlorobiphenyl was quantitated only to a limited extent. Dichlorobiphenyl makes up about 25% of Peak 2 of an Aroclor 1242 standard; Peak 1 is a dichlorobiphenyl peak, but due to poor reproducibility and the inability to accurately quantitate it in samples, especially samples with any interferences, Peak 1 was not evaluated in the historic analyses. However, since the difference in mono and dichlorobiphenyls between historic cores and current cores will be used to assess the extent of in situ dechlorination of PCBs, it is important to evaluate the integrity of the archived samples and extracts with regard to these homologs. Therefore, the reproducibility of these peaks must be evaluated in order appropriately interpret the PCB congener data.

As indicated previously, it is not the purpose of the packed column analysis to demonstrate the accuracy or precision of the original sampling, extraction, or analytical procedures. Rather, the packed column analyses are meant to establish the integrity of the archived sample or sample extract from the time the archived sample or extract was generated to the present. Therefore, the historic chromatograms will be reviewed (by Dr. Bopp) for the presence of Peak 1, as well as other identifiable early eluting peaks which correspond to (on a retention time basis) to mono and dichlorobiphenyls. Mono- and di-chlorobiphenyl peaks present in the historic chromatogram (including Peak 1, Webb and McCall relative retention time [RRT] 21; also Webb and McCall RRT 16 [dichlorobiphenyls] and RRT 11 [monochlorobiphenyl]) should be present in the current chromatogram at a relative composition (see 6.3.2) of at least 50% of that identified in the historic chromatogram.

5.2.4.3.4 Retention Time Criteria

Relative retention times (RRTs) of individual packed column peaks will be compared for Peaks 2 through 22 (as defined in Bopp, 1979) for the current packed column analysis relative to the calibration standard RRTs must agree within $\pm 2\%$.

5.2.4.3.5 Aroclor (Standard) Calibration Criteria

Quantitation of the individual peaks based on the Aroclor standards must agree between the historic and current analyses to within 5% RPD. This criterion is meant to establish comparability of the Aroclor standards used in both the historic and current analyses, so that evaluations are not altered due to variations in homolog/congener composition of Aroclor standards used to quantitate packed column peaks in the original analysis as opposed to those used by Aquatec in 1993. If this criterion is met, then quantitation can proceed without any correction or adjustment. A preliminary review of Aroclor standards currently used by NYSDEC indicates good reproducibility; therefore, it is expected that this criterion will be met. However, if this criterion is not met, and the current laboratory cannot obtain standards which adequately reproduce the historical standards, then peak quantitations will be corrected for the differences so that apparent differences between the two data sets are not attributable to the difference in the composition of available Aroclor standards.

5.2.4.4 Comparability of Radionuclide Data

The ability to make appropriate comparisons of historic sediment data to current sediment data is also dependent upon being able to identify the same sediment deposition year in both cores. This is done by the radionuclide data, which have been generated for both the archived and current sediment cores. Radionuclide dating for both the historic and current cores was performed at Lamont-Doherty Earth Observatory (LDEO), so differences attributable to laboratory or method variablity are not expected.

While no strict numerical criteria have been established for the comparison of the historic to current radionuclide data, the factors to be evaluated include the following:

- Both cores should have Cesium-137 profiles which follow a pattern consistent with historical events (discussed in greater detail in Section 6.3)

- The Cesium profiles for the core years occuring in both cores (i.e., the year of collection of the archived core back to 1954, if both cores were deep enough) should match well
- The rate of deposition, as estimated by the depth (length of core) between distinct events in the radionuclide chronology, should be relatively constant. It should be noted that this factor is not as critical; if differences in deposition rates are evident between the historic and current core, then other parameters, such as potassium-40 data (an indicator of silica or sand content) and weight loss on ignition data (an indicator of total organic matter content) will be evaluated to assess the comparability of the cores.

5.2.5 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. Deficiencies in the data may be due to sampling techniques, poor accuracy or precision, or laboratory error. While these deficiencies may affect certain aspects of the data, usable data may still be obtained from applicable samples. Completeness is of the utmost concern for Phase 2B samples. For the high resolution sediment core current/archived sample comparisons, the selection of several sample pairs from each coring location increases the chances of obtaining at least some usable data from each location, even if part of the data is unusable. For the archived water samples, completeness is addressed via the number of samples to be analyzed.

In order for useful conclusions to be drawn from the GC/ECD PCB congener analyses of the archived samples, an adequate number of data points must be available. However, the minimum completeness goal for PCB Aroclor sample integrity (i.e., those archived samples which pass the comparability/reproducibility screening discussed in Section 5.2.4) is matrix-dependent. For archived water column samples (water and suspended matter), the goal is between one-third and one half of the samples (the lower goal [one-third] is applicable if higher completeness is achieved for certain key stations, such as Troy). For the archived sediment extracts and samples, the completeness goal is on a core-by-core basis. The goal is at least three good (comparable) analyses from each core for which four or five analyses have been planned. If less than this number of samples pass the comparability screening, insufficient comparisons of current to historic congener data can be made from which to draw meaningful or defensible conclusions. In such a case, none of the samples from that core will be subject to PCB congener analysis.

5.2.6 Sensitivity

Quantitation limit goals for the laboratory analyses planned for the Phase 2B archived sample analysis effort are shown on Tables 5-3 and 5-4 of this SAP/QAPjP. Quantitation limits may be affected by matrix interferences, such as those caused by high concentrations of non-target analytes (e.g., sulfur or high molecular weight organics), or trace impurities in analytical reagents concentrated to detectable amounts in the analytical process. To control interferences in the laboratory, only pesticide grade or better solvents will be used, and method blanks must be demonstrated to be free of contamination prior to analysis. For PCB congener analyses, sample/extract cleanups will be performed (specified in the Appendices) to achieve the specified detection limits. No further cleanup of the archived extracts will be performed; the PCB fraction extracts will be analyzed "as is", except for reconstitution to make up for evaporation (described more fully in Section 6.5). The archived pesticide fraction extracts which will be analyzed for PCB congeners (to improve the accuracy of the mono- and di-chlorobiphenyl data, as discussed above in Section 5.2.2) will be subject to silica gel cleanup (Section 7.12 of Appendix A-3) to remove interfering pesticides and improve sensitivity. If the quantitation limits are still not achievable, the usability of the data, with respect to meeting the Phase 2B objectives, will be evaluated.

5.3 Procedures for Monitoring PARCC Parameters

PARCC parameters will be monitored through the use of procedures which have been referred to in Section 5.2. These procedures will include the use of laboratory method blanks, field duplicates (where available) and laboratory duplicates, matrix spike blanks, matrix spike samples, duplicate matrix spikes, matrix spike blanks, surrogate spikes, performance evaluation samples, laboratory control samples, and a careful examination of calibration and check standards. Comparability of data sets is also evaluated through specific programs aimed at establishing the reproducibility of data generated previously as compared to data generated with the sampling, extraction, and analytical procedures developed and utilized for the current investigation. Matrix spike blanks (which are equivalent to Laboratory Control Samples [LCSs] for PCB analyses) and performance evaluation (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.

Table 5-1

Accuracy and Precision Objectives for Reproducibility of Packed Column Gas Chromatographic Analyses

	Total PCB Recovery*	Peak/Homolog Abundance*	MS and MSD Recovery	PE sample Recovery***	Surrogate Recovery
Dried Sediment	50% RPD	80 - 120%**	60 - 150%	60-150%	60 - 150%
Dried Filters	50% RPD	80 - 120%**	60 - 150%	60-150%	60 - 150%
Hexane Extracts	40% RPD	80 - 120%**	60 - 150%	75-125%	75 - 125%

* Based on comparison to previous (historical) data, using the same quantitation procedure used in the historical data reporting.

** For all peaks present at 10% or greater of largest peak (based on peak height). Criterion for peaks present at 2% to 10% of largest peak is $\pm$2% (absolute). See Figures 5-1 for example chromatograms showing peak designations for individual Aroclor standards 1242, 1254, and 1260.

*** PE Sample recovery will be calculated in accordance current EPA calculation procedures (i.e., as per CLP SOW OLMO1.0, as revised) unless otherwise specified by the PE sample provider. So that the PE sample remains blind to the analytical laboratory, this calculation must be done by the data reviewer; the analytical laboratory will only be required calculate the concentrations of PE samples in accordance with the procedures in Appendix A-11. The PE sample recovery limits shown are default limits; acceptability will be determined by performance-based criteria specified by the PE sample provider, where available. The PE sample will be Aroclor 1242 if available.

Table 5-2

Accuracy and Precision Objectives for Capillary Column Gas Chromatographic Analyses

Parameter	Matrix	Field Duplicate Precision (% RPD)	MS/MSD[1] Precision (% RPD)	LCS[2] Accuracy (% Recovery)	MS/MSD Accuracy (% Recovery)	Surrogate Accuracy (% Recovery)
PCB Congeners	Extracts	40[4]	40	60-150	60-150	60-150[3]
	Particulate	50	40	60-150	60-150	60-150[3]
	Sediment	50	40	60-150	60-150	60-150[3]

[1] Five or ten percent of PCB congener analyses will be confirmed by GC/ITD (Appendix A-5 of the Phase 2A SAP/QAPjP) with criteria of <50% RPD between methods.

[2] LCS = MSB (matrix spike blank) for PCB congener analysis.

[3] Surrogates are tetrachlorometaxylene (TCMX) and octachloronaphthalene.

[4] Extract precision criterion based on laboratory duplicate analysis.

NA = Not Applicable

Table 5-3

Detection Limit Goals for Packed Column GC PCB Peaks

Peak or Aroclor	Detection Limit Goal
RRT 11 and RRT 16	None (1)
Peak 1	40 ppb (1)
Peaks 2 and 3	20 ppb
Peaks 4 through 15	10 ppb
Peaks 16 through 22	4 ppb
Decachlorobiphenyl	2 ppb

(1) Due to anticipated low concentrations and sample interferences, evaluation of Peak 1 and earlier eluting peaks is not expected to be possible in most samples or extracts in the packed column analysis.

Table 5-4

Detection Limit Goals for PCB Congeners
by Capillary Column Gas Chromatography

Matrix	Homolog	Detection Limit Goal
Hexane Extracts	Monochlorobiphenyl	5 ng/ml hexane *
	Dichlorobiphenyl through Hexachlorobiphenyl	1 ng/ml hexane *
	Heptachlorobiphenyl through Decachlorobiphenyl	1-2 ng/ml hexane *
Suspended Matter (Filters)	Monochlorobiphenyl	5 ng/filter
	Dichlorobiphenyl through Hexachlorobiphenyl	1 ng/filter
	Heptachlorobiphenyl through Decachlorobiphenyl	1 - 2 ng/filter
Dried Sediments	Monochlorobiphenyl	2 ug/kg
	Dichlorobiphenyl through Hexachlorobiphenyl	0.5 ug/kg
	Heptachlorobiphenyl through Decachlorobiphenyl	0.5 - 1 ug/kg

* Actual sample detection limits will vary depending on the dry weight (for sediment and suspended matter) or volume (for water) of the sample originally extracted. For sediments, based on the 2 to 5 gram sample typically analyzed by Bopp, and a 1 ml final extract volume, the sample detection limits will range from about 0.5 ug/kg to 1.0 ug/kg per congener (except for monochlorbiphenyls). For 10 liter water samples (assuming a 1 ml final extract volume), the corresponding sample detection limit goals are .0001 ug/l to .0002 ug/l.

Table 5-5
Packed Column Analysis Evaluation Criteria

1. **Total PCB Evaluation Criterion:**

   Current packed column analysis and historic quantitation must quantitate to within ±50% RPD (as total PCBs) of the original analysis, using the same calculation procedure as was used for the historic analysis.

2. Peak Abundance (Distribution) Criteria

   2.1 Determine Largest Peak in the initial chromatogram

   2.2 Evaluate initial chromatogram for major peaks; major peaks are defined as all peaks present at 10% or more of the largest peak.

   2.3 Calculate the relative distribution of each major peak present in the initial chromatogram.

   2.4 Calculate the relative distribution of each major peak in the current analysis; use the same major peaks as determined for the historic analysis.

   2.5 Calculate the RPD between the relative distribution for the historic analysis (determined in step 2.3 above) and the current analysis (determined in step 2.4 above) for each major peak.

   2.6 The RPD criterion is 20% for each major peak.

3. Low Molecular Weight Peak Evaluation

   3.1 Inspect the initial historic chromatogram for the presence of Peak 1 and other identifiable early eluting peaks corresponding to monochlorobiphenyls and dichlorobiphenyls (i.e., RRT 11 and RRT 16).

   3.2 Inspect the current chromatogram for the presence of the same peaks determined to be present and identifiable in the historic chromatograms (step 3.1, above).

   3.3 If any low molecular weight PCB peaks are present, calculate the relative abundance of low molecular weight peaks, relative to the largest peak in the historic chromatogram, for both the historic and current analyses.

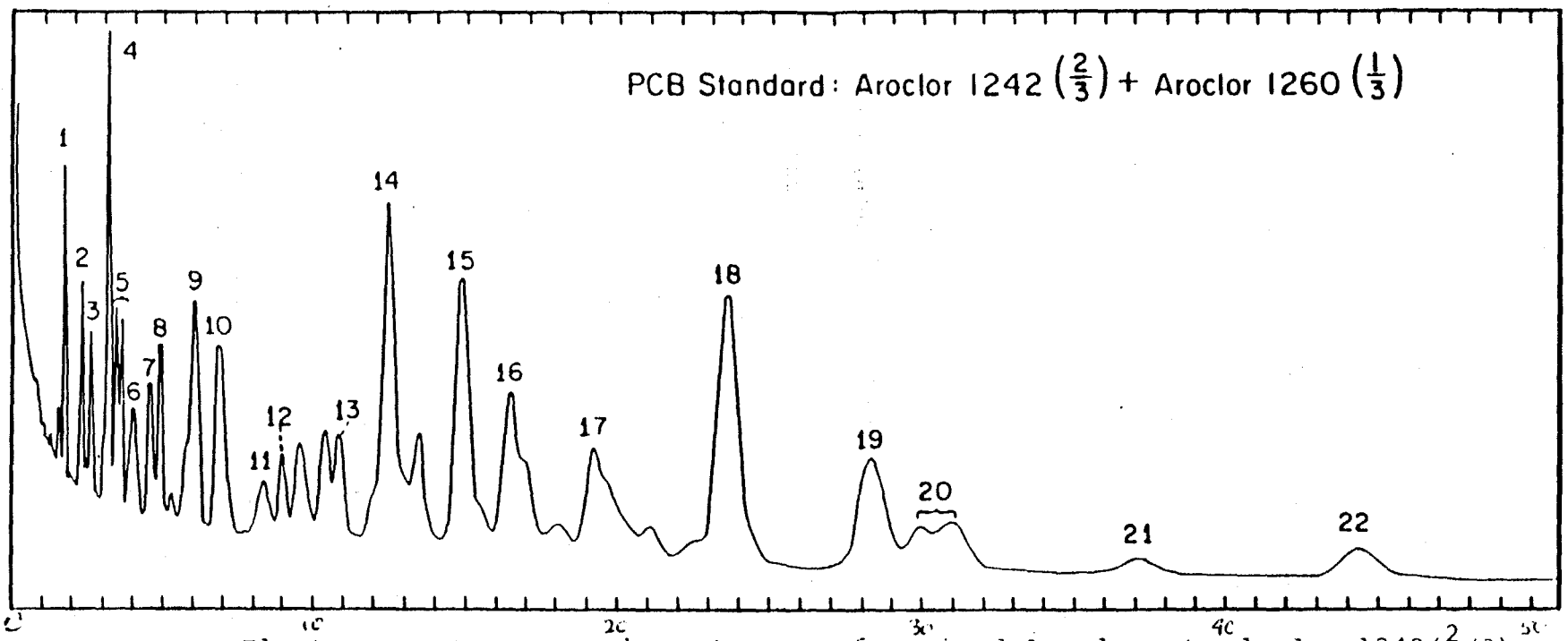
   3.4 The evaluation criterion is that the current chromatogram should have low molecular weight peaks present at least 50% of their relative abundance in the historic chromatogram.

Figure 5-1

Packed Column Chromatogram of Mixed Aroclor Standard

Showing Peak Numbering System

(From Simpson, Bopp, Warren, Deck, and Kostyk, 1984)



Electron capture gas chromatogram of a mixed Aroclor standard: 1242(2/3) plus 1260(1/3). Peak numbering follows that of Bopp et al., 1981.

6 Sample Selection and Preparation

This section describes the sample selection process and outlines the sample handling procedures for the archived sample analysis program. Details on laboratory analysis procedures are provided in the appendices. The sample selection processes for the archived sample analysis program are defined for each of the archived media to be analyzed. Each archived sample will be evaluated on two sets of criteria. The first set concerns sample selection for packed column (Aroclor) analysis based on sample documentation and sample archiving and storage integrity; the second set of criteria concerns the selection for capillary column (PCB congener) analysis based on the results of the packed column analysis. The procedures used for the initial collection, archiving, and storage of the archived samples are summarized in Section 6.1 The criteria for the selection of archived water samples for packed column analysis are given in Section 6.2. The criteria for the selection of archived sediment samples for packed column analysis are given in Section 6.3. Section 6.4 contains the criteria for the selection of a sample for capillary column (congener) analysis based on the comparison between the current and historic packed column analyses.

It is important to note that the criteria given in Sections 6.2 and 6.3 are designed to provide a basis sufficient to evaluate the integrity of an archived sample. These criteria are not intended to provide a basis for the use of the original quantification. Once the integrity of the sample has been shown to meet the appropriate criteria based on the packed column analysis, the PCB congener concentrations in the sample will be determined by capillary column GC/ECD analysis. For this reason, the criteria listed in these sections are considered documentation goals. The sample may still be considered acceptable for analysis even if it does not satisfy every evaluation criterion. Final sample selection will be made by TAMS' project manager in consultation with the program team.

6.1 Collection, Archiving, and Storage of Archived Samples

In order to assess the applicability of the PCB congener data from analysis of the archived samples and extracts, it is necessary to have an understanding of the procedures under which the samples were collected, archived, and stored. Ideally, comparability of historic to current data is maximized where procedures involved in the data generation are essentially identical; however, even where procedures were not similar, useful data may be obtained as long as the differences are understood and inappropriate comparisons between data sets are not made.

6.1.1 Initial Collection of Archived Samples

The archived sediment core samples were obtained in a manner essentially identical to that used for the high resolution coring program for this reassessment RI/FS. The core samples were taken either by hand or gravity coring at the approximate locations indicated in Table 3-2. All of the historic sediment samples were archived (i.e., homogenized, dried, and sealed in aluminum cans) prior to analysis.

Archived suspended matter (particulate filter) samples were generated in two ways. Many of the particulate samples (all of those from 1977 through about April 1983, and some of the later ones as well) were generated in the laboratory by filtering a 10 or 20 liter (nominal volume) river water sample through a glass fiber filter (Whatman GFF, 0.7 micron effective pore size). The apparatus and process used for filtering was similar to that used for the current RI/FS; some minor differences (e.g., the historic samples were filtered under slight pressure of pure nitrogen gas, as opposed to zero air for the current program) do not materially affect the nature of the filtration. Beginning in 1983, a second filtration process was also used. A large volume filter sampler (LVFS) was used to collect the suspended matter in situ. The LVFS consists of a submersible pump, filter holder, and flow meter mounted in an aluminum frame. Suspended matter was collected on a 10-inch diameter filter (1.2 micron quartz fiber, Whatman QMA, was used for most samples; a glass fiber filter was used for some samples) suspended in at least 8 feet of water.

Archived dissolved phase water sample extracts proposed for reanalysis in this program exist only through April, 1983; i.e., only for those samples which were laboratory filtered in the manner described above. In some cases, no dissolved phase water samples were collected in conjunction with the LVFS-generated suspended matter samples. Samples proposed for analysis from the Fort Miller and Rexford (Mohawk) locations in 1983, along with all water column samples proposed from 1984, 1985, and 1986, exist only as suspended matter extracts and unanalyzed filters.

6.1.2 Archiving and Storage of Archived Samples

As noted above, sediment samples were archived prior to the original analysis. The archiving process consists of homogenizing each individual core slice, drying the samples in a PCB-free environment at about 30 to 35° C and then storing in an air-tight aluminum can. The drying and canning of the samples facilitated the radionuclide counting that was done at the time. Samples which were analyzed were opened, a 1 to 5 gram aliquot

removed for extraction and analysis, and the cans were re-sealed. These archived sediment samples have been stored at LDEO at ambient temperature until the present. Most samples have been stored in PVC-lined aluminum cans, although some sediment samples have been stored in 30-ml glass vials with teflon screw caps. Two extracts were also generated for each sediment sample - a hexane extract which contained the PCBs and p,p'-DDE, and a methylene chloride extract (solvent-exchanged to hexane) which contained the remaining pesticides (and which later data has shown also contains some of the monochlorobiphenyl PCB congeners). These extracts have been stored in a freezer at -8° C in 6-ml screw-cap glass culture tubes at Lamont-Doherty Geological Observatory (now the Lamont Doherty Earth Observatory) since the initial extraction. The volume of the extract in the vial was marked on the vial at the time the extract was placed into storage. For the sediment core samples, the archived samples include the dried, canned sediment, the PCB fraction extracts, and the pesticide fraction extracts.

The suspended matter samples which were generated from laboratory filtration of 10 or 20 liter whole water samples exist only as extracts; the samples (filters) were consumed in their entirety in the extraction process. The whole water samples were typically stored from 2 to 10 days prior to filtration (Bopp, Simpson, and Deck, 1985, p. 45). As with the sediment extracts, the suspended matter extracts exist as both a hexane (PCB) extract and a methylene chloride (pesticide) extract, and have been stored in the same manner as the sediment extracts.

The LVFS suspended matter samples consisted of 10-inch diameter filters. At least two, but usually four, filters were generated for each sample. For analysis, an entire filters was usually extracted, although in some cases a filter was cut in two prior to extraction. For the LVFS samples, the archived material consists of the two extract fractions, as well as unanalyzed filters, and the part of the filter from which a slice was removed for analysis. The unanalyzed filters have been stored in sealed containers at ambient temperature at LDEO.

The 10 or 20 liter dissolved phase water samples were consumed in their entirety in the extraction process; only extracts exists for these samples. Dissolved phase water sample extracts exist only for archived samples collected 1986; only archived LVFS suspended matter samples exist subsequently. The two extract fractions for the dissolved phase water samples have been stored in the same manner and location as the other extracts described above.

6.2 Sample Selection Criteria for Archived Water Column Samples for Packed Column Gas Chromatography

The selection of archived water column sample extracts for analysis under this program is largely contingent upon the integrity of sample storage and the quality of the records associated with each sample. Historic water quality data on PCB congener levels are useful throughout the Hudson River and are particularly valuable in the Upper Hudson area. Emphasis has been given to samples from the Hudson above the salt front (i.e., north of about RM 55). Given the limited availability of the archived water samples, it is expected that most of the extant Upper Hudson archived samples, along with selected Lower Hudson samples (as listed in Table 3-1), which meet the following criteria will be analyzed:

1. The sample container appears intact and contains at least 25% of the original extract volume.
2. Field records exist documenting date, time and location of sample collection.
3. Laboratory records exist documenting date and time of analysis as well as the following information:
   a. Chromatogram(s) of the sample analytical run showing retention times.
   b. Chromatograms of the standard analytical runs showing retention times.
   c. Documentation of the Aroclor concentrations in the standards used.
   d. Documentation of the preparation of laboratory standards.
   e. Documentation of reference standards used.
   f. Documentation of the calculation procedures used to quantify sample contaminants.
   g. Results of quantification calculations including:
      - peak heights or areas
      - peak retention times
      - calculated contaminant concentrations
   h. Analytical procedure used, including:
      - column type(s) (packing, support, diameter, length, etc.)
      - detector type
      - temperature program
      - other chromatographic conditions (e.g., gas flow rates)
      - injection volume
      - extraction/concentration procedure

- sample/extract cleanups performed

It assumed that the available documentation of these items will vary among samples and sample groups. In addition, the importance of a given sample to the program goals will vary depending upon the date of sample collection, its location and the number of contemporaneous samples near the sample location. The ultimate decision concerning the selection of a given sample for analysis must take into account the criteria listed above. Each sample will be reviewed in light of these considerations with the final selection to be made by the project team. As shown on Figure 3-1, it is estimated that approximately 57 water column extracts or filters may be analyzed in this program.

Once a water or suspended matter sample (as a hexane extract) has been selected and has satisfied the criteria given above, it will be analyzed via packed column gas chromatography. It is expected that many of the archived extracts will have partially evaporated during storage; these samples will be reconstituted to their original extract volume prior to analysis, as discussed in Section 6.5. The procedure for packed column gas chromatography is described in Appendix A-11. The quality control criteria for the analysis are given in Chapters 5 and 11 and in Appendix A-11. The results of this analysis will be compared with the original analytical results to evaluate the sample integrity. The evaluation criteria are discussed in Section 5.2.4.

For those suspended matter samples that exist only as dried particulates on a filter, it will not be possible to confirm sample integrity beyond satisfying the documentation criteria (i.e., no historic analysis exists for comparison purposes). These samples will be extracted via the program standard extraction technique given in Appendix A-3 and analyzed for PCB congeners only via capillary column gas chromatography only, discussed in Appendices A-4 and A-5. (This procedure is only applicable in the event that it is necessary to analyze particulate filters, instead of or in addition to extracts.)

6.3 Sample Selection Criteria for Archived High Resolution Sediment Core Samples for Packed Column Gas Chromatography

The selection of archived high resolution sediment core samples for this program will be based on a more extensive set of criteria than that for the water column samples. Each archived sediment sample must meet all of the criteria given in Section 6.2. Additional criteria are required, however, in order to permit the direct comparison

between matched pairs of current and archived sediment samples. Both the archived sediment core and the current sediment core must satisfy certain criteria.

Each of the archived sediment samples being considered for this analysis program was collected as part of a historic high resolution sediment core. As part of the current high-resolution coring program, selected historic sites were re-occupied and cored with the assistance of the scientists from LDEO and RPI who collected the historic cores. As discussed in Section 3, the goals of this analysis program require that each archived high-resolution sediment core sample accurately match a current high-resolution sediment core sample based on location and on time of deposition. Thus, before any archived sediment samples can be selected, an analysis of the current high resolution core must be completed and meet the following criteria:

1. The historic site must be successfully re-occupied and cored as part of the current high resolution sediment coring program.
2. The current core must be subdivided into sediment intervals which approximate those of the historic core.
3. The current core must yield a radionuclide chronology which also closely approximates that obtained for the historic core, after allowing for additional deposition and sediment compression in the intervening time. (See discussion of comparability in Section 5.2.4.4.)
4. The results of the PCB analyses performed on the current core sample intervals must meet the project QA/QC criteria for PCB analysis (as defined in the applicable project SAP/QAPjP and appendices). It should be noted that it is unlikely that formal data validation of the current high resolution core sample data will be completed prior to the analysis of the archived samples. Therefore, a less rigorous review will be conducted by the QAO (or designee) to evaluate compliance with this criterion.

These criteria are designed so that the current high resolution sediment core will provide the needed data for comparison to the archived sediment samples before beginning the archived sample analysis.

After satisfying these criteria, it then necessary to match the radionuclide chronologies of the historic and current high resolution sediment cores on a location by location basis (e.g., the radionuclide chronology of the historic core from river mile 143 would be matched to the current core collected at river mile 143). Once the core chronologies are matched, approximately five archived sediment samples (intervals, or slices) from each historic

high resolution core will be selected. In general, these samples will correspond to the following radionuclide/time horizons, determined from radionuclide and other data:

1.	1954-1956	Appearance of Cesium-137
2.	1963-1964	Cesium-137 maximum, corresponding to the end of the atmospheric atomic weapons testing.
3.	1973-1976	PCB concentration maximum (1973 dam removal and 1975 flood).
4.	1977-1986	Time of historic core collection. (This corresponds to the uppermost core layer in the historic core. The depth of the corresponding layer in the current core will be estimated based on its radionuclide chronology assuming a constant rate of sediment accumulation between major radionuclide horizons.)
5.	~1971	Cobalt 60 maximum corresponding to a major Indian Point nuclear power facility release. (This interval is limited to cores from the Lower Hudson below RM 60.)

For core locations above the salt front (above RM 55), a fifth or sixth core interval may be selected from a radiologically distinct region of the radionuclide spectrum present in both cores. This interval will be selected based on the degree of similarity between the current and archived cores. An example of the core intervals showing the correlation between PCB concentration and year of sediment deposition (as determined from the radionuclide chronology) is shown in Figure 6-1.

Once selected, the archived sediment core extracts and samples will be subject to the same criteria concerning sample documentation as the archived water samples. Thus, the criteria are as follows:

1. The sample extract container appears intact and contains at least 25% of the original extract volume. For sediment samples which are to be re-extracted, the container must appear intact and contains the recorded sediment mass.
2. Field records exist documenting date, time and location of sample collection.
3. Laboratory records exist documenting date and time of analysis as well as the following information:
   a. Chromatogram(s) of the sample analytical run showing retention times.
   b. Chromatograms of the standard analytical runs showing retention times.

c. Documentation of the Aroclor concentrations in the standards used.

d. Documentation of the preparation of laboratory standards.

e. Documentation of reference standards used.

f. Documentation of the calculation procedures used to quantify sample contaminants.

g. Results of quantification calculations including:

- peak heights or areas
- peak retention times
- calculated contaminant concentrations

h. Analytical procedure used, including:

- column type(s) (packing, support, diameter, length, etc.)
- detector type
- temperature program
- other chromatographic conditions (e.g., gas flow rates)
- injection volume
- extraction/concentration procedure
- sample/extract cleanups performed

The level of available documentation for these items will vary among sediment samples/extracts and sediment cores. In addition, the importance of a given sample to the program goals will vary depending upon the date of sample collection, its location and the number of similar core sample pairs from the sample location. The ultimate decision concerning the selection of a given sample for analysis must take into account the criteria listed above. Each sample will be reviewed in light of these considerations with the final selection to be made by the project team.

Once a sediment sample has been selected based on the criteria given above, the archived hexane extract will be analyzed via packed column gas chromatography. The archived dried sediment will be analyzed for this purpose only if the extract does not meet the selection criteria; the procedure for sediment extraction for subsequent packed column analysis of these samples is given in Appendix A-10. This extract (i.e., the archived extract, or the dried sediment or particulate matter extract from A-10, which duplicates the technique used by Bopp) is largely free of the pesticide DDT and its derivative DDD. It also yields an incomplete extraction of the monochlorobiphenyls (based on the results of the MDL study completed for the current high resolution sediment coring program, monochlorbiphenyl recovery is estimated to be about 75%). It is necessary to replicate this extraction process in

order to evaluate the sample integrity (i.e., to allow comparison of the chromatograms generated at the time of the original analysis to those generated from the current packed column analysis of archived samples).

The procedure for packed column gas chromatography of the archived extracts and the extracts produced by the procedure given in Appendix A-10 is described in Appendix A-11. The quality control criteria are given in Chapters 5 and 11 and in Appendix A-11. The results of this analysis will be compared with the original analytical results to evaluate the sample integrity. If the review of the packed column chromatogram indicates adequate reproducibility in accordance with the criteria specified in Section 5 (see Table 5-5), the sample extract will then be analyzed for PCB congeners. The evaluation criteria (for determining archived sample or extract integrity) are discussed briefly below.

6.4 Archived Sample Selection Criteria for PCB Congener Analysis by Capillary Column Gas Chromatography

This section discusses the criteria for selecting samples for capillary column gas chromatography based on the historic records and the results of the packed column analysis. Essentially the criteria consist of two types, absolute quantitation criteria and relative concentration criteria. These criteria will be applied to both the archived sediment samples and the archived water sample extracts. The results for the packed column analysis will be compared to the original packed column analysis on an individual peak basis and an Aroclor basis. These criteria define the general level of precision and accuracy needed to satisfy the archive sample analysis goals. These criteria are summarized on Table 5-5. There are five criteria for reproducibility, including: total PCB Quantitation; relative peak abundance; low molecular weight congeners; retention time; and Aroclor standard calibration. The details of these criteria have been previously discussed in Section 5. However, final selection of samples will be left to the discretion of the program members. The precision objectives given above are guidelines and samples may be selected which satisfy most but not all of these criteria but may be needed to meet the program goals.

Tables 3-1 and 3-2 summarize the analyses to be completed as part of the archived sample analysis program.

6.5 Sample Containers, Preservation, and Holding Times

No field sampling is required in this program and the archived samples have been prepared for long term storage, so holding times until extraction and sample preparation do not apply here. However, for the purposes of expediting the program, archived sediment samples should be extracted for the packed column analysis within 5 days of verified time of sample receipt (VTSR). Analysis of the sediment extracts (both archived extracts being reanalyzed along with newly-generated extracts using the procedure in Appendix A-3) will be required within 20 days of VTSR. Water sample extracts must be analyzed by the packed column technique within 20 days of VTSR. Dried suspended matter samples must be extracted for GC/ECD analysis within 5 days of VTSR. Analysis by the GC/ECD and GC/ITD procedures for all samples must be completed within 40 days of VTSR.

6.6 Preparation of Sampling Equipment and Containers

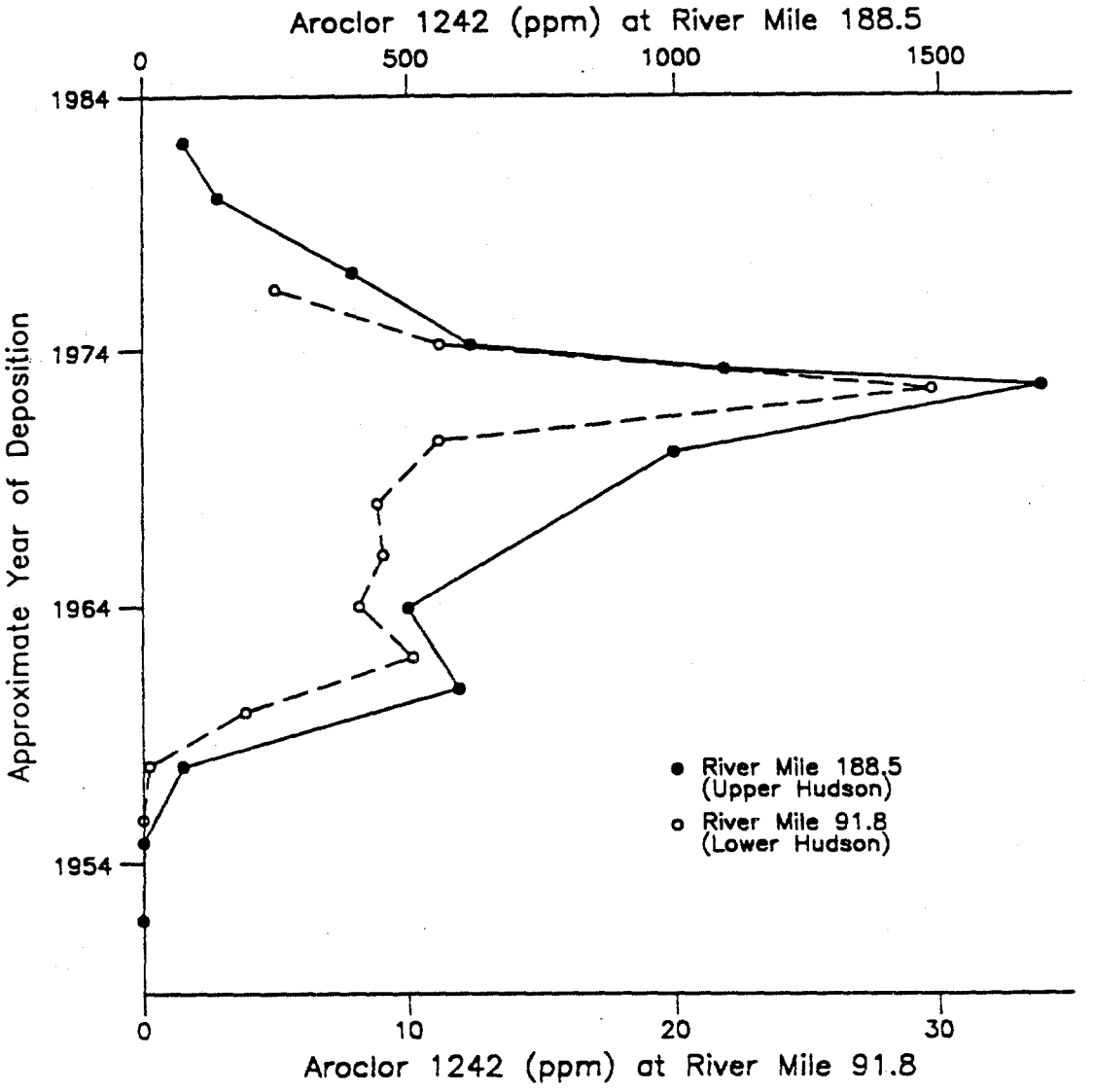
No field sampling will be performed as part of this program so this section is not applicable to the current work being conducted under this SAP/QAPjP. Archived extracts have been stored in 5-ml glass vials. Archived sediment and suspended matter samples have been stored exclusively in 10 and 20 ounce PVC-lined air-tight aluminum cans.

Samples will be packaged for shipment and dispatched to the laboratory (by hand delivery or by commercial delivery service) for analysis. Chain of custody procedures are detailed in Section 7.0 of this SAP/QAPjP. Sample and extract temperatures will be maintained during shipping at the same temperature at which they have been stored.

Figure 6-1

Aroclor 1242 Concentration vs. Approximate Year of Deposition for Two Hudson River Cores

Year of Deposition Established by Radionuclide Analysis



Source: Bopp et al. (1985).

TAMS/*Gradient*

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" (USEPA, 1986). This custody is in three parts: sample collection; 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 six months after completion of the final report.

It should be noted that complete custody documentation is not available for the archived samples. Custody documentation will be recreated from available records, such as field logbooks and laboratory notebooks. This is discussed further in Section 7.2.1, below. These documents will be retained as part of the final evidence file.

7.1 Sample Identification

In order to properly track all samples collected for the archived sample 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-000-0000-A

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

The first two characters represent the sampling effort. For the sampling effort, all samples will be labelled AS for archived suspended matter samples (filters or extracts); AC for archived core (extracts or dried sediment) samples, and AW for archived water sample extracts.

For the archived core (AC) samples, the first three digits represent the core number, with the archived core being assigned a number (001 through 027) corresponding to the matching current high resolution core location designation. The first digit will be "0" for extracts; if substitution of the dried sediment is necessary (see discussion Section 5.2.5), it will be designated by "9". For example, AC-915 would be the archived dried sediment core from station 15; AC-015 would be the archived dried sediment extract from core location 15. The first two digits of the last four digits represent the midpoint of the depth of the core slice in centimeters, and the last two digits of this sequence are the year. For example, the 20 to 24 cm deep core slice extract collected in 1979 from location 15 would be designated as AC-015-2279.

For both the archived water samples and the archived filter samples, the first three digit sequence includes a sample type identifier (first digit) and a station location identifier (second and third digits). The sample types are identified as 10 or 20 liter laboratory filtered through a glass fiber filter (designated "0"); or field filtered in situ (large volume filter sample) through a quartz fiber filter (designation "1") or through a glass fiber filter (designated "2"). For the filters which have not been extracted (applicable to suspended matter [AS] samples only), the designations are 6 (for laboratory glass fiber filter), 7 (field quartz fiber filter) and 8 (field glass fiber filter). The station location identifiers are the same as for the current water transect sampling program, and are shown on Table 7-1. The last four digit sequence represents the month and year of sample collection; for example, 1086 would indicate a sample collected in October 1986.

As was the case for previous sampling efforts, the final letter is reserved for QC sample designations where applicable - D for Duplicate, and M for Matrix Spike or Matrix Spike Duplicate.

7.2 Field Specific Custody Procedures

For the archived samples, the custody procedures are broken down into two parts. These are the historical (initial) custody procedures which were implemented at the time of collection, and the more rigorous custody procedures which will be initiated for the analyses to be conducted under this SAP/QAPjP.

7.2.1 Initial Custody Procedures of Archived Samples

As discussed in Chapter 6, the archived samples proposed for analysis were collected over a 10 year period (1977 to 1986) for research purposes and not for enforcement; therefore, the custody procedures utilized at the time of collection, and during subsequent handling, storage, and analysis, do not meet current NEIC procedures. Historical custody will be recreated from available records, such as field and laboratory notebooks, as well as interviews with personnel involved in the initial sampling and analysis (several of whom are members of the current project team). The QAO will review the available custody records and documentation and evaluate whether adequate records exist to justify inclusion of a particular sample in the archived sample analysis program.

Written documentation will be recorded for all historical custody information obtained by interviews with personnel involved in the initial sampling and analysis. This documentation will be signed and dated by both the prerson(s) providing the information and recording the information. A copy of documentation of information relevant to the recreated custody will be placed in the final evidence file.

7.2.2 Initiation of Current Custody Procedures

A formal chain of custody will be established for the archived extracts or samples beginning with the removal of the samples from storage to shipping containers. An example of the chain-of-custody form proposed for use is shown as Figure 7-1. The date the samples are packaged for shipment or delivery to the laboratory (whether delivered by hand or by commercial delivery service) will be considered the date of sample collection for this phase of the project. 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.

Packaging and shipping procedures will be as follows:

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

- All bottles will be tagged with sample numbers and locations (see Section 7.1).

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

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. The original (i.e., historical) sample identification will also be listed on the form. When transferring the possession of samples, the individuals relinquishing and receiving shall sign, date, and note the time on the record. This record documents transfer of custody of samples from the sample manager to another person, to the analytical laboratory, or to/from a secure storage area.

- It is planned that samples will be delivered in person by the sample manager. However, if the samples are sent by common carrier, an airbill or bill of lading will be used. Receipts of bills of lading 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.

- 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. Custody seals will not be required for samples hand-delivered by project personnel.

- Archived sample extracts which have been stored in a freezer (i.e., at temperatures of less than 0° C) will be packaged for shipment to the laboratory so as to maintain this temperature (e.g., on dry ice). Samples (sediment or filters) which have been stored at ambient temperatures will be shipped at ambient temperature.

- 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 sample manager.

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 or cans
- Presence of all samples listed on the chain of custody form
- Bottle labels match chain of custody
- Presence of ice and temperature of the cooler (not applicable to archived sediments)
- Number of containers (coolers) received matches number shown on airbill (not applicable to hand-delivered samples)

The sample custodian will fill out a Shipment Condition Inspection Report (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 chain of custody form. The sample custodian will then sign and date the chain of custody form. This date will be considered the verified time of sample receipt (VTSR) for the purpose of tracking holding times.

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 chain of custody form, inspection report, and airbill (if applicable) will then be forwarded to the laboratory project manager.

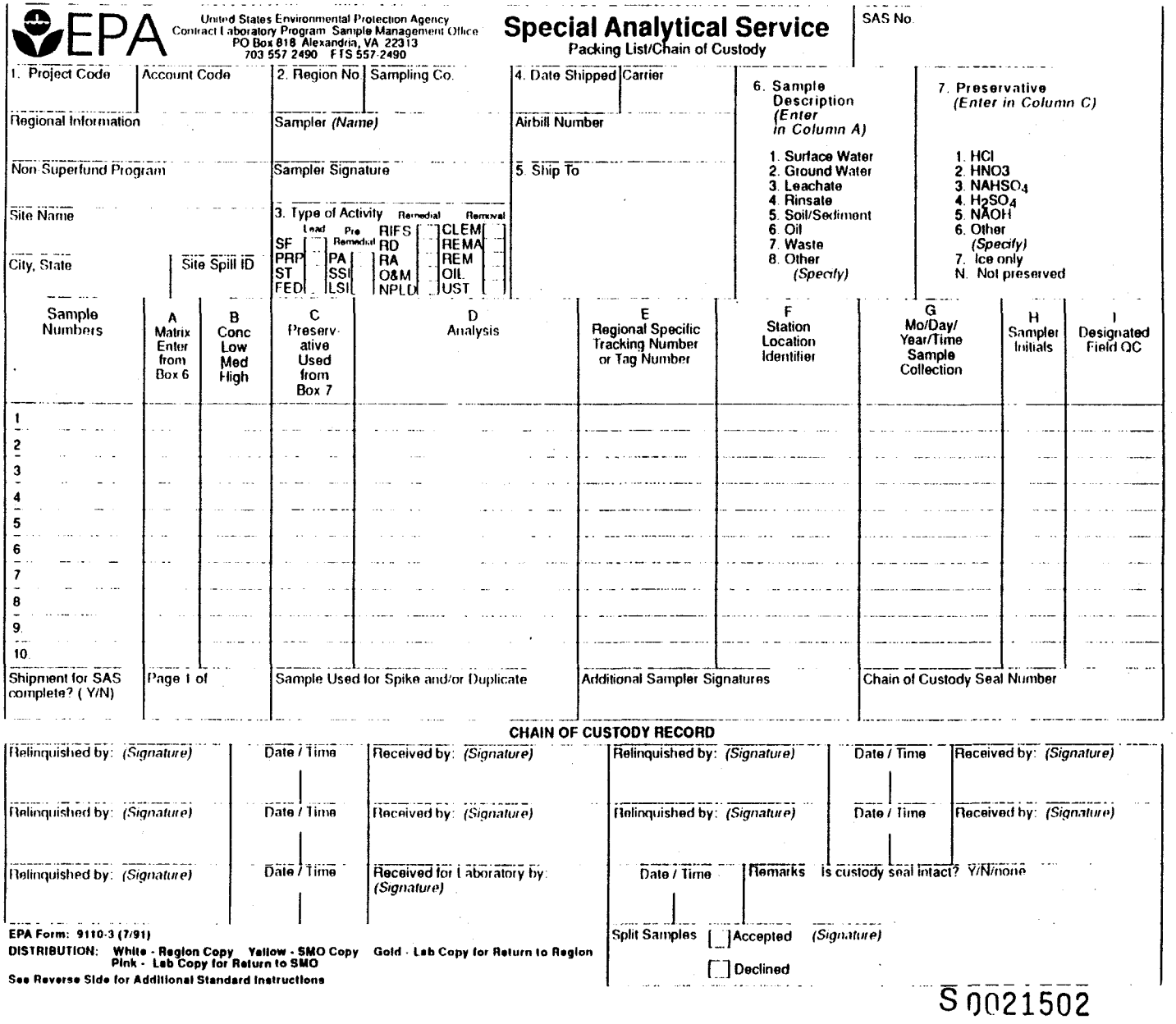
The laboratory project manager or designee will inspect the paperwork. If problems are noted, the laboratory project manager will resolve them with the TAMS sample manager or quality control coordinator.

After log-in, samples will be placed in refrigerated storage (extracts at $< 0°$ C; archived sediments or filters in cans do not require refrigeration until the samples are opened) 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 laboratories, 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; and pictures. Copies of previous records relating to the original sampling and analysis of the archived samples and extracts will also be part of the project record. Persons involved in the long-term custody (storage) shall prepare records indicating the storage and custody of the samples and stating that the samples have not been tampered with. Documentation to be included in the final evidence file for the archived sample analysis explicitly includes relevant documentation used to establish historical custody, which may include (but is not limited to), copies of field logbooks and field notes from the intital sample collection; laboratory logbooks or bench sheets from the initial analysis; and signed documentation of interviews documenting information from personnel involved in any aspect of the historical sampling, analysis, or custody.

Any unused portions of samples or extracts will be re-sealed and returned to LDEO (except for extracts of dried sediments and filters prepared by the Phase 2 laboratory; these extracts will be retained by the laboratory for the normal duration according to CLP requirements [1 year]). Chain-of-custody procedures and documentation will be maintained and continued during the return of archived samples and extracts to LDEO. All reports will be retained by EPA Region II.



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
Regional Information
Non-Superfund Program
Site Name
City, State | Site Spill ID

2. Region No. | Sampling Co.
Sampler *(Name)*
Sampler Signature
3. Type of Activity — Remedial: Lead (SF, PRP, ST, FED); Pre Remedial (PA, SSI, LSI); RIFS, RD, RA, O&M, NPLD. Removal: CLEM, REMA, REM, OIL, UST

4. Date Shipped | Carrier
Airbill Number
5. Ship To

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. HNO3
3. $NAHSO_4$
4. H_2SO_4
5. NAOH
6. Other *(Specify)*
7. Ice only
N. Not preserved

Sample Numbers	A Matrix Enter from Box 6	B Conc Low Med High	C Preservative Used from Box 7	D Analysis	E Regional Specific Tracking Number or Tag Number	F Station Location Identifier	G Mo/Day/ Year/Time Sample Collection	H Sampler Initials	I Designated Field QC
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									

Shipment for SAS complete? (Y/N) | Page 1 of | Sample Used for Spike and/or Duplicate | Additional Sampler Signatures | Chain of Custody Seal Number

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)*
Relinquished 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: 9110-3 (7/91)
DISTRIBUTION: White - Region Copy Yellow - SMO Copy Gold - Lab Copy for Return to Region
Pink - Lab Copy for Return to SMO
See Reverse Side for Additional Standard Instructions

TAMS/*Gradient*

S 0021502

FIGURE 7-1
EXAMPLE CHAIN-OF-CUSTODY FORM

FIGURE 7-2

SHIPMENT INSPECTION REPORT FORM

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:	_____	_____	_____
	OK	Not OK	Not Checked

Other _____: _____ _____

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

Problems and Comments

_____

_____

_____

_____

_____

_____ _____
Signature Date

8 Calibration Procedures and Frequency

Since this SAP/QAPjP covers the analysis of previously collected samples and sample extracts, no field calibration will be performed.

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 appendices:

Parameter	Appendix/Reference
Extraction and cleanup of archived sediments and filters	A-10 of this SAP/QAPjP
Packed column GC PCB Aroclor analysis	A-11
PCB Congener Analysis (GC/ECD)	A-4
PCB Congeners (GC/ITD confirmation analysis)	A-5
Cleanup of Archived Pesticide Extracts for GC/ECD analysis	A-3 (Section 7.12)

Silica gel used for sample cleanup (Appendix A-3 and Appendix A-10) must be calibrated each time a new batch is prepared in order to determine the optimum hexane elution volume.

The packed column GC Aroclor 1242 calibration standards will include three early eluting peaks (RRT 11, RRT 16, and Peak 1) which contain monochlorobiphenyl congeners and dichlorobiphenyls in order to establish the retention time and response factor for these analytes, which were not targeted in the historical analysis. These peaks will be calibrated using calibration factors derived from the Webb and McCall composition data (Appendix A-11, Table 2) and the Aroclor 1242 calibration, as specified in Appendix A-11.

9 Analytical Procedures

The archived sample investigation consists solely of laboratory analyses will be performed for PCBs. Initial PCB analysis will be for PCB peaks or Aroclors by packed column GC, followed by PCB congener analysis by GC/ECD and confirmation by GC/ITD. The flowchart for the analytical sequence is shown in Figure 9-1. 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. Table 9-3 provides a cross-referencing between PCB homologs and peak number for the packed column GC analysis. The detection limit goals for the PCBs are defined in Section 5.

9.1. Reconstitution of Archived Extracts

As noted previously, it is likely that partial evaporation of the extracts may have occurred. Prior to reanalysis of extracts (including reanalysis by packed column GC), samples will be reconstituted to the calibrated marking spot marked on the screw top vial. Each approximately 5-ml vial will be visually inspected to determine how much, if any, of the extract has evaporated. If noticeable extract loss is evident, the cap will be unscrewed, and the extract will be brought back to the original volume by the addition of pesticide grade hexane added by a disposable pipet. Extracts which have been stored refrigerated or frozen will be allowed to equilibrate (while still in sealed vials) to ambient temperature prior to reconstitution and analysis. Disposable pipets will be decontaminated prior to use by rinsing with pesticide-grade hexane.

9.2 PCB Congener Analysis by Capillary Column GC/ECD

After the packed column results have been reviewed in the context of the criteria given in Section 5 (see Table 5-5), the archived extracts or samples meeting the criteria will be analyzed for PCB congeners by capillary column gas chromatography.

For the archived water samples which exist as extracts, no further sample preparation of the PCB fraction extracts is required, and these extracts can be analyzed by the procedure for capillary column gas chromatograph analysis using an electron capture detector (GC/ECD) given in Appendix A-4. The pesticide fraction extracts will be subject to the silica gel cleanup procedure specified in Section 7.12 of Appendix A-3. The extracts (both the

archived PCB fraction extract and the cleaned up archived pesticide fraction extract) will be spiked with the surrogates TCMX and OCN (or BZ #192); these surrogates will serve as retention time markers. Approximately 5% of the water samples will also be analyzed using a capillary column gas chromatograph with an ion trap detector (GC/ITD) as described in Appendix A-5.

For the archived sediment samples, the original hexane extract prepared for packed column gas chromatography will be analyzed for PCB congeners using the capillary column procedure (GC/ECD) given in Appendix A-4. As with the archived water column sample extracts, the pesticide fraction extract will be subject to silica gel cleanup. The archived sediment extracts (both the PCB and cleaned up pesticide fractions) will be spiked with the surrogates TCMX and OCN (or BZ #192); these surrogates will serve as retention time markers. If any archived dried sediment samples are analyzed, they will be spiked with these surrogates prior to extraction. Archived dried sediment samples will be reconstituted to approximately 20% water (by weight) with PCB-free water at the analytical laboratory prior to extraction. Approximately 10% of the samples will be analyzed using a capillary column gas chromatograph with an ion trap detector (GC/ITD) as described in Appendix A-5. [The pesticide fraction will also be analyzed by GC/ECD, and the results will be mathematically combined.]

As discussed previously, the archived suspended matter samples which exist as dried sediments will be extracted by the method given in Appendix A-3 before analysis by capillary column gas chromatography (GC/ECD) as described in Appendix A-4. Archived extracts will be spiked with surrogates prior to analysis; archived filters will be spiked with surrogates prior to extraction. Approximately 5% (but at least one) of these samples will be analyzed by the GC/ITD method given in Appendix A-5. Sample preparation for packed column analysis is not required for samples for which no historic analytical (packed column) data exists.

Table 9-1

Analytical Procedures

Parameter	Method	Appendix
PCB Congeners	Capillary column GC/ECD	A-4
PCB Congener Confirmation	GC/ITD	A-5
PCB Aroclors/Total PCBs	Packed column GC/ECD	A-10, A-11
Pesticide Fraction Extract Cleanup	Silica Gel	A-3 (Section 7.12)

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

PEAK/HOMOLOG CORRELATION FOR PACKED COLUMN GC ANALYSIS [1]

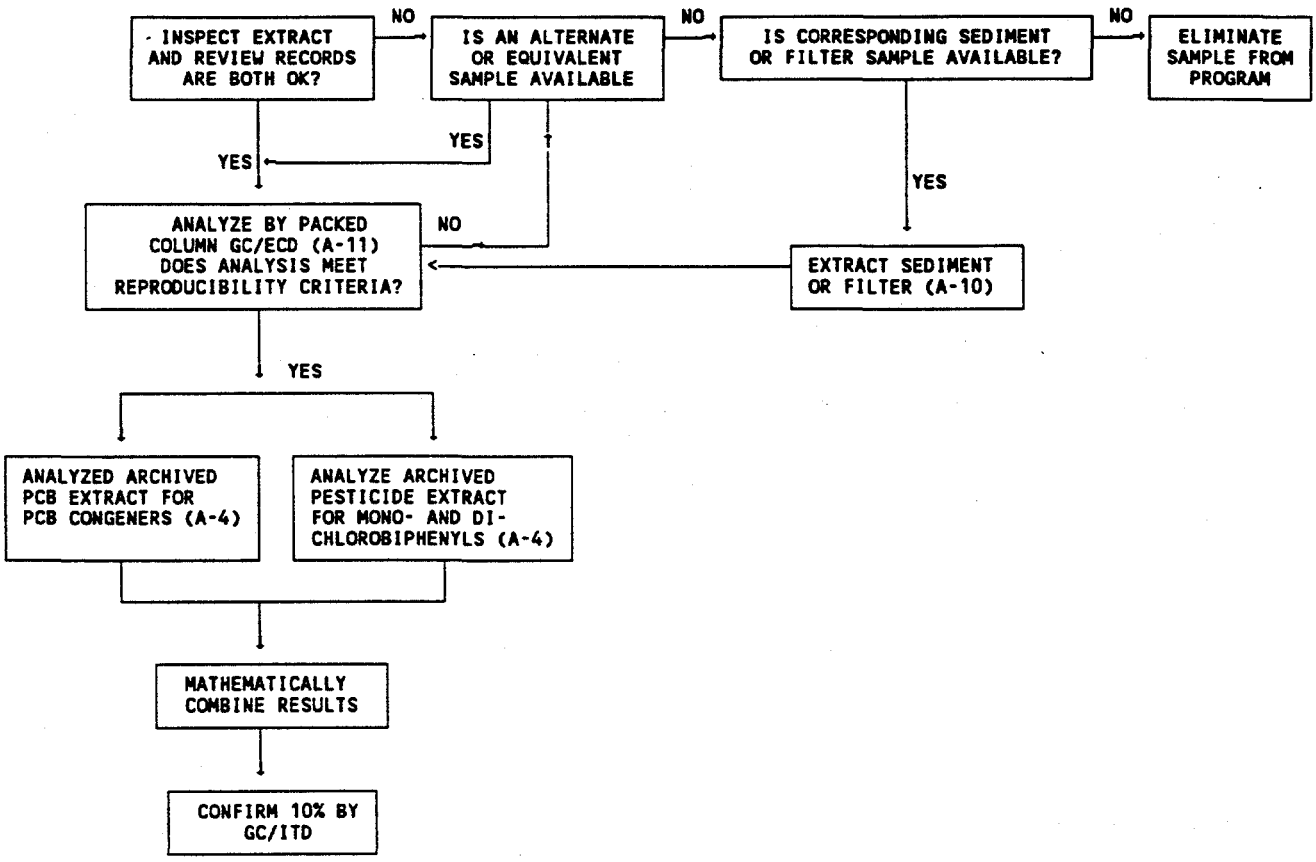
PEAK #	RRT	AROCLOR 1242 HOMOLOG	AROCLOR 1254 HOMOLOG	AROCLOR 1260 HOMOLOG
–	11	Monochlorobiphenyl [2]	— [3]	— [4]
–	16	Dichlorobiphenyl	— [3]	— [4]
1	21	Dichlorobiphenyl	— [3]	— [4]
2	28	25% Dichloro, 75% Trichloro	— [3]	— [4]
3	32	Trichlorobiphenyl	— [3]	— [4]
4	37	Trichlorobiphenyl	— [3]	— [4]
5	40	Trichlorobiphenyl	— [3]	— [4]
6	47	Tetrachlorobiphenyl	Tetrachlorobiphenyl	— [4]
7	54	33% Trichloro, 67% Tetrachloro	Tetrachlorobiphenyl	— [4]
8	58	Tetrachlorobiphenyl	Tetrachlorobiphenyl	— [4]
9	70	90% Tetrachloro, 10% Pentachloro	25% Tetrachloro, 75% Pentachloro	Pentachlorobiphenyl
10	84	57% Tetrachloro, 43% Pentachloro[6]	Pentachlorobiphenyl	Pentachlorobiphenyl
11*	98	Pentachlorobiphenyl	Pentachlorobiphenyl	60% Pentachloro, 40% Hexachloro
12	104	Pentachlorobiphenyl	Pentachlorobiphenyl	Co-elutes with Peak 11
13	125	85% Pentachloro, 15% Hexachloro	70% Pentachloro, 30% Hexachloro	15% Pentachloro, 85% Hexachloro
14	146	75% Pentachloro, 25% Hexachloro	30% Pentachloro, 70% Hexachloro	Hexachlorobiphenyl
15	174	— [5]	Hexachlorobiphenyl	Hexachlorobiphenyl
16	203	— [5]	Hexachlorobiphenyl	10% Hexachloro, 90% Heptachloro
17	232	— [5]	Heptachlorobiphenyl	10% Hexachloro, 90% Heptachloro[7]
18**	280	— [5]	— [3]	Heptachlorobiphenyl
19**	332	— [5]	— [3]	Heptachlorobiphenyl
20**	372	— [5]	— [3]	Octachlorobiphenyl
21**	448	— [5]	— [3]	Octachlorobiphenyl
22**	528	— [5]	— [3]	Octachlorobiphenyl
Decachlorobiphenyl		— [5]	— [3]	— [4]

* p,p'-DDE coelutes with Peak 11 in packed column analysis.
** Peaks 18 through 22 are present in commercial Aroclor 1260 and are expected to be significant in the lower Hudson only.
RRT = Relative Retention Time (p,p'-DDE = 100).

Notes:
(1) Based on analysis on 3% SE-30 on 80-100 mesh Gas Chrom Q, 2 mm ID, 2 meter column; homologs determined from GC/MS data. Composition and RRT data from Webb and McCall (1973).
(2) Monochlorobiphenyls elute prior to Peak 1, but were not quantitated or identified in the original analysis. Monochlorobiphenyls will be identified and quantitated to the extent feasible in the reanalysis by packed column GC and chromatogram reproducibility criteria will include evaluation of monochlorobiphenyl data (see Table 5-5).
(3) Peak not reported present in Aroclor 1254
(4) Peak not reported present in Aroclor 1260
(5) Peak not reported present in Aroclor 1242
(6) Weighted average of two peaks at RRT 78 and RRT 84. RRT 78 not reported present in Aroclor 1254 or 1260.
(7) Coelutes with RRT 244 (Aroclor 1260 only). Composition is at center of RRT 232.

This table is adapted from Webb and McCall (1973). Peak numbering system after Bopp (1979) and Bopp et al. (1981).

Figure 9-1
Analytical Sequence Decision Tree and Flow Chart



10 Data Reduction, Validation, and Reporting

Field notebooks for archived samples, custody documents, and laboratory reports generated for this project will be filed and stored. Copies of original documents pertaining to the initial collection and analysis of the archived samples will be retained where the originals are not available (e.g., because these documents are the property of others); however, the originals will be reviewed and the a record of the locations of the originals will be kept by TAMS. These documents are tracked during a periodic inventory during audits performed under the direction of the TAMS/Gradient Quality Assurance Officer (QAO) of the project, Dr. A. Dallas Wait. Abbreviations employed in this section are defined in Section 18.

As discussed in Section 3, a two phased approach will be taken toward generation of the data. The first phase consists of verifying the integrity of the existing archived samples and extracts. This will be achieved by visual inspection of extracts and samples, review of sampling, analytical, and custody records, packed column GC Aroclor analysis, and comparison of the results with the historical data, both quantitative and qualitative. The evaluation of the packed column results will be used to determine if it is appropriate to proceed to the next stage, PCB congener analysis by capillary column GC/ECD.

The system for data reduction and reporting is summarized in Figure 10-1.

10.1 Data Reduction

The analyst who generates the analytical data has the prime responsibility for the correctness and completeness of the data. 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), including verification that the correct peaks have been used for Aroclor identification and quantitation;
- 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
- Analytical 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 Packed Column GC PCB Data Evaluation

The objective of the packed column GC PCB analysis is to determine the integrity of the archived samples and extracts. For this purpose, the primary criterion is the reproducibility of the original analytical chromatograms and results. Since this analysis is in effect a screening analysis to determine if it is appropriate to proceed with PCB congener analysis, rigorous validation of this data will not be performed. Data will be reviewed to see if it meets the acceptance (comparability) criteria specified in Section 5 (Table 5-5). A completeness review will also be performed to verify that sufficient supporting data and documentation have been provided. Data for which the current data is not comparable (similar) to the original analysis (i.e., do not meet the comparability criteria listed on Table 5-5) will be reviewed to see if the problem can be traced to laboratory problems in the current analysis. This review may include inspection of the chromatograms (historic and current), checking of calculations, and review of the procedures used and QC data. If the review (by TAMS/Gradient) indicates that the non-comparability can be attributed to problems with the current analysis (i.e., current analysis was not in conformance with the methods or criteria specified in Appendix A-11), the laboratory may be requested to re-extract or reanalyze the sample or extract. If there is no apparent flaw in the current analysis, or if corrective action fails to generate a current analysis comparable to the historic analysis, samples for which the current packed column GC analyses do not reproduce the original (historical) analysis will not be submitted for PCB congener analysis.

A written record of the results of each current/historical packed column analysis evaluation will be prepared by TAMS/Gradient for each sample analyzed.

10.3 PCB Congener Analysis Data Validation

Data validation is the process of reviewing data and accepting, qualifying, or rejecting it on the basis of sound criteria. The PCB congener data generated during this program will be validated according to guidelines in this SAP/QAPjP (Appendices A-6 and A-7). 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 the supporting data using professional judgment in areas not specifically addressed by the 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 (Appendix A-7).

It is important that quantitation limits be kept as low as possible for PCB congener analyses. It is expected that the quantitation limit goals defined in Section 5 will be met. Precision and accuracy requirements have been defined in Section 5. Guidelines for acceptable surrogate standard recoveries, spike recoveries and RPD of duplicates in both waters and particulates have been defined in the analytical appendices (A-4 and A-5) and the evaluation procedures for assessing these recoveries in Appendices A-6 and A-7.

10.4 Data Reporting

Different reporting formats will be utilized for the packed column GC Peak/Aroclor data and for the capillary column PCB congener data. These are discussed in greater detail below.

10.4.1 Packed Column GC Aroclor Data Reporting

In order to evaluate the reproducibility of the current data with regard to the historical data, the following items (as a minimum) must be included in the report:

- All data must be quantitated on an individual peak basis, and a total PCB value will also be reported derived from Peak data (Appendix A-11). In addition, for data originally quantitated on an Aroclor basis, quantitation of PCBs as Aroclors, using the peaks identified in the packed column analytical SOP (Appendix A-11). For data originally quantitated on a "peak 6-derived" basis as total PCBs, quantitation as per Bopp, Simpson, and Deck (1985).
- Chromatograms of each sample analysis
- Identification and peak height calculation for each peak on the chromatogram, and identification of peaks used for Aroclor quantitation
- Final analyte concentration.
- Laboratory sample ID#, and client sample ID#
- Final volume of extract or prepared sample.
- Preparation or extraction and analysis dates for holding time verification.
- Calibration information, including (where applicable):
  - Calibration factor for each peak
  - % RSD calculations for each initial calibration

- concentration response data of the calibration check standards.

- Amount of surrogate spiked and percent recovery and retention time shift of each surrogate.
- For matrix spike samples, the amount spiked and % recovery of each peak or Aroclor spiked.
- For matrix/analytical duplicate or spike duplicate samples, % RPD calculated for each compound or analyte.
- Blank results for method blanks and laboratory analytical blanks.
- Raw data and preparation and extraction logs must include:
  - analyst initials and date
  - initial and final sample volumes or weights
  - matrix analyzed (extract, sediment, or filter); extracts analyzed must identify original sample matrix and weight/volume extracted
  - amount and concentration of stock spike solutions added to MS/MSD samples
  - Vendor or Lot Number identification for all Aroclor standards and true value concentrations of these standards
- All raw data analysis printouts and logs must include:
  - analyst initials and date
  - Model Number and type of instrument (including GC column) used for analysis
  - conditions of instrument (e.g., column/detector temperatures, nitrogen flow rates, etc.)
  - time of start of analysis of each sample and QC sample, time of end of analysis
  - Analytical method reference
  - dilutions performed and amount of sample analyzed or injected
  - calibration standards labeled and time recorded
  - QC samples and blanks clearly labeled.

Results should be reported on a Form I-equivalent, modified to list the results for each of the 25 resolvable peaks as the target analytes, as well as the total PCB concentration, calculated from the sum of the individual PCB peaks. Peaks not found to be present should be included in the Form I, with the calibrated quantitation limit (CQL) and the qualifier "U" (not detected). The matrix analyzed, as well as the original sample matrix, should also be on this form. The remaining information provided should be the same as provided on the CLP Form I. For samples analyzed as extracts, the laboratory should report the extract concentration (e.g., as ug PCB/ml extract) and also calculate and report the concentration based on the original sample matrix (e.g., ug/kg sediment; ug/l water; ug/filter), based on the sample size or sample volume data provided to the laboratory by TAMS.

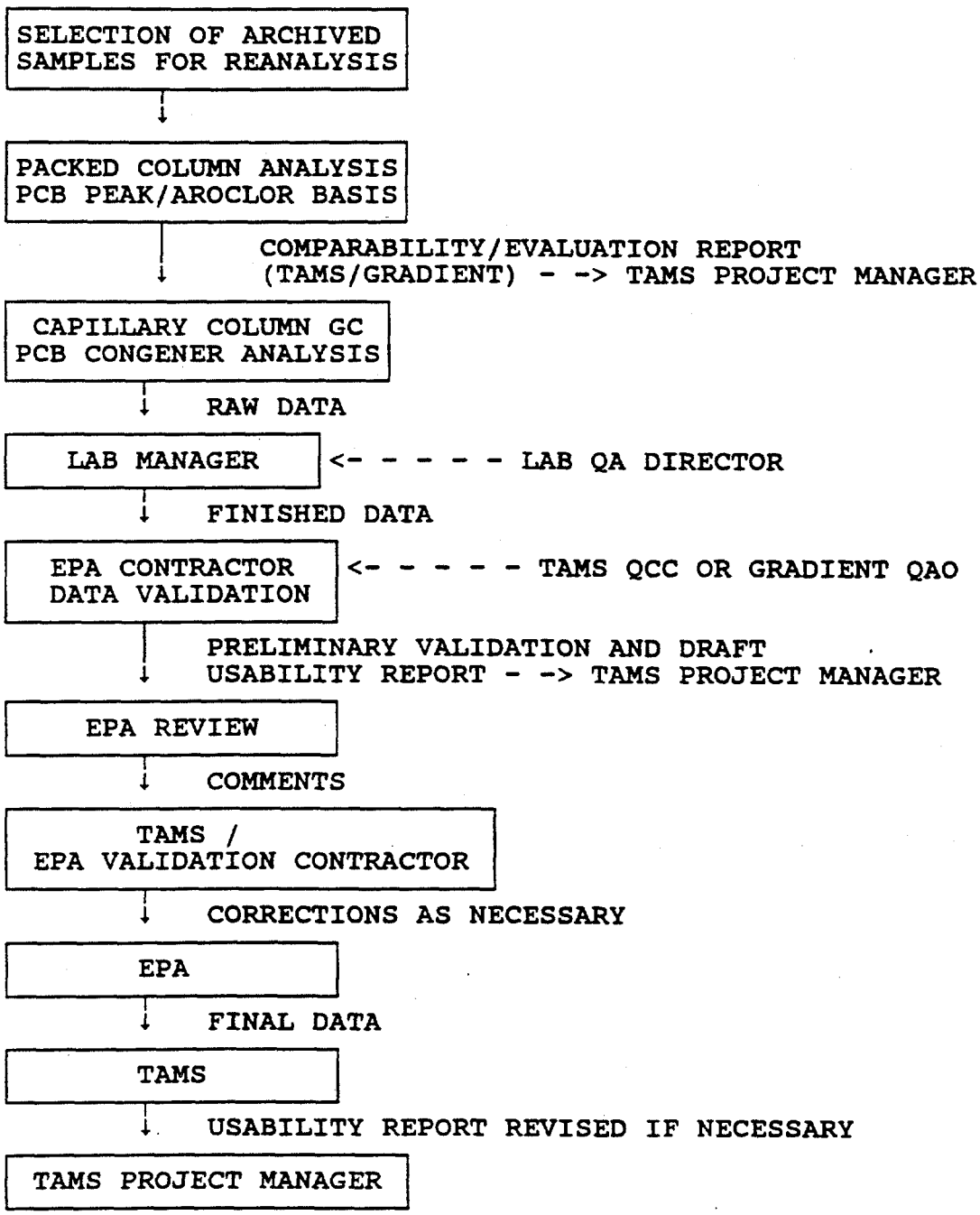
10.4.2 PCB Congener Data Reporting

For PCB congener data, appropriate CLP forms (SOW OLM01.8 or current version, modified as necessary) for pesticide/PCB reporting should be used where applicable. The specific deliverables are defined in the applicable SOP (Appendix A-4). QC, supporting, and raw data documentation equivalent to full CLP deliverables 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#, client sample ID#, location.
- 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 first and second column chromatography including chromatograms.
- Quantitation reports for first and second columns for each congener and surrogate.
- Amount of surrogate spiked and percent recovery of each surrogate.
- For matrix spike samples, the amount spiked and % recovery of each congener spiked.
- For matrix/analytical duplicate or spike duplicate samples, % RPD calculated for each congener.
- For matrix spike blanks (equivalent to laboratory control samples), true values and percent recovery of each congener quantitated.
- Blank results for method blanks and laboratory analytical blanks.
- Raw data and preparation and extraction logs must include:
  - analyst initials and date
  - initial and final sample volumes or weights
  - matrix analyzed (extract, sediment, or filter); extracts analyzed must identify original sample matrix and weight/volume extracted
  - amount and concentration of stock spike solutions added to MS/MSD or LCS samples
  - Vendor or Lot Number identification for all initial and continuing calibration standards and true value concentrations of these check standards.

- All raw data analysis printouts and logs must include:
  - analyst initials and date
  - Model Number and type of instrument (including GC column) used for analysis
  - conditions of instrument (e.g., column/detector temperature, etc.)
  - time of start of analysis for all samples and QC samples, time of end of analysis
  - Analytical method reference
  - dilutions performed and amount of sample analyzed or injected
  - calibration standards labeled and time recorded
  - QC samples and blanks clearly labeled.

FIGURE 10-1
PROTOCOLS FOR DATA REDUCTION AND REPORTING:
LABS CONTRACTED TO TAMS



11 Internal Quality Control Checks

The type and frequency of Quality Control (QC) checks are summarized in Tables 11-1 and 11-2. Method SOPs (Appendices A-3, A-4, A-5, A-10, and A-11) must be referenced for more detailed information.

11.1 Field Quality Control Checks

This part of the project consists of analysis of samples already collected (archived samples). No field sampling will be conducted specifically for this phase of the project. Therefore, field quality control checks (field blanks, field duplicates, and analyte-free water blanks) typically instituted as part of a field sampling program will not be collected or analyzed.

11.2 Matrix Specific Quality Control

Matrix-specific QC will consist of analysis of matrix spike (MS)/matrix spike duplicate (MSD) samples. A MS/MSD pair will be performed for PCB Aroclor and PCB congener analysis at the frequency of one per 20 samples (5%) per matrix, or one per Sample Delivery Group (SDG, defined as each 20-sample set), whichever is more frequent.

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. The 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. Matrix (analytical) duplicates will also be analyzed on both packed on capillary columns to compensate for the lack of field duplicates for the archived samples. The RPD between the sample and MD concentrations are determined and compared to the criteria specified in individual SOPs and in Table 5-1.

11.3 Laboratory Quality Control Checks

Table 11-2 lists the frequency of laboratory QC checks. Accuracy and precision criteria for LCS, MS/MSD are given in Section 5. Matrix (analytical) duplicates will be analyzed to compensate for the lack of field

duplicates. 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.

  Method blanks will be prepared and anlyzed for both packed and capillary column analyses conducted under this program. In addition, archived blanks will be reconstituted and reanalyzed, to the extent that such blanks still exist. If archived blanks no longer exist, the records of blank analyses performed along with the original analyses will be evaluated to assess the possiblility of false positives or interferences resulting from contamination in the initial extraction and analysis of the archived samples.

- **Performance Evaluation (PE) Samples**

  PE samples will be submitted blind to each laboratory performing PCB congener analyses every 3 to 6 months. Arrangements for the provision of PE samples will be made through USEPA Region II MMB. If PE samples are not available from EPA, a commerically available sediment PE sample which is a NIST Standard Reference Material (SRM) is available for PCB congeners and will be used as the PE sample for capillary column GC/ECD analysis of archived sediment samples. A PCB congeners in hexane PE sample will also be submitted. A PCBs as Aroclors PE sample will also be submitted for for packed column analysis for the dried sediment matrix. PE samples will be included in the first shipment of archived samples to the laboratory; if all samples are shipped simultaneously, the laboratory will be instructed to include the PE sample in the first analytical SDG.

- **Matrix Spike Blanks**

  For each parameter and matrix (as applicable; see Tables 11-1 and 11-2), a minimum of one matrix spike blank, equivalent to a laboratory control sample (LCS) will be analyzed for every 20 samples. The LCS will be used to access laboratory performance of the method. The matrix

spike blank for PCB congener analysis will be spiked with the same standard spike mix as used for MS Samples.

- **Matrix Spike/Matrix Spike Duplicate**

  For both packed and capillary column PCB analysis, a minimum of one MS/MSD pair per matrix per batch of 20 samples or per SDG to assess accuracy and determine matrix effects.

- **Matrix Duplicates**

  For both packed column Aroclor analysis and capillary column GC/ECD PCB congener analysis, whenever field duplicates are not available, a minimum of one matrix (laboratory) duplicate (MD) pair per matrix per batch of 20 samples or per SDG to assess precision.

- **Surrogate Standards**

  Surrogate standards to estimate recoveries (for PCB congeners) and to account for sample-to-sample variation as required in the PCB method. Surrogates will serve as retention time markers for packed column analysis of PCB peaks.

- **Initial Calibration**

  For capillary column PCB congener analysis, 5-point multilevel initial calibrations of instruments to establish calibration curves. For packed column PCB analysis, calibrations will consist of a three-point calibration using separate standards of Aroclor 1242, Aroclor 1254, and Aroclor 1260/decachlorobiphenyl.

- **Continuing Calibration**

  A continuing calibration check will be performed every 12 hours for capillary column PCB congener analysis. For packed column PCB analysis, calibration checks (OCAL) every 12 hours.

- **Second Column Confirmation**

  All PCB samples for capillary column congener analysis will be analyzed on a secondary capillary column for PCB congener confirmation. (Packed column PCB analysis is on a single column only.)

- **Confrirmation of congeners by GC/ITD**

  Approximately 10% of the sediment samples (5% of the water column samples) analyzed for PCB congeners will require additional confirmation by GC/ITD (Appendix A-5). The GC/ITD analyses will be performed with the same capillary column used for the GC/ECD analyses, and will employ similar congener standard mixes. The GC/ITD analyses are intended to confirm congener identification. Quantitative deviations in the results of the two methods (GC/ECD *vs* GC/ITD) should be less than 50 percent.

TABLE 11-1
LABORATORY QUALITY CONTROL SUMMARY

	Quality Control Parameters									
Laboratory Parameters	**Method**	**ICV**	**ICB**	**CCV**	**CCB**	**MB**	**MSB**	**MS**	**MSD**	**MD**
PCB congeners - GC/ECD	P1			X	X	X(1)	X	X	X	X(2)
PCB Congeners - GC/ITD	P2			X						
PCB Aroclors - Packed column GC	P3			X	X	X(1)		X	X	X(2)

Note:

(1) Analysis of method blanks will also include analysis of historical (archived) method blanks, to the extent such blanks are available.

(2) Matrix (analytical) duplicates will be analyzed to the extent necessary to make up for the unavailaibliy of field duplicates.

Methods:

P1 = Project specific method for PCB congeners by capillary column gas chromatography/electron capture detection (Appendix A-4)

P2 = Project-specific method for PCB congener confirmation gas chromatography/ion trap detection (Appendix A-5)

P3 = Project-specific method for PCB Aroclors by packed column GC/ECD (Appendix A-11)

General Notes:

For PCB congeners by capillary column GC/ECD, the MSB serves as the LCS. See method SOP and section 11 for specific requirements. For packed column PCB peak/Aroclor analysis, the instrument blank serves as the CCB; and the OCAL serves as the CCV. The quality control parameters are defined in Table 11-2.

Table 11-2

Quality Control Frequency Summary

For tests that specify the following Quality Control (QC), this table summarizes the frequency requirements. See method SOPs and Table 11-1 for applicable QC per parameter.

QC Sample Type	Frequency
Initial Calibration Verification Check (ICV)	Not required for PCB Aroclor or congener analysis
Initial Calibration Blank (ICB)	Not required for PCB Aroclor or congener analysis
Continuing Calibration Verification Check (CCV)	Every 12 hours during analytical run for PCB Aroclors and PCB congeners (= continuing calibration check, or OCAL)
Instrument Blank (equivalent to Continuing Calibration Blank, or CCB)	Every 12 hours for PCB congeners (CCB) and Aroclors (Instrument Blank).
Matrix Spike Blank (MSB) (equivalent to Laboratory Control Sample, or LCS)	1 per 20 or SDG whichever is more frequent (for PCB congener analysis only. Not required for packed column PCB Aroclors analysis.
Matrix Spike (MS)	1 per 20 or SDG whichever is more frequent
Matrix Spike Blank (MSB)	1 per 20 or SDG, whichever is more frequent, for PCB congener analysis only; MSB = LCS.
Matrix Spike Duplicate (MSD)	1 per 20 or SDG whichever is more frequent (PCB congener analysis only)
Matrix Duplicate (MD)	Not required for PCB Aroclor or congener analysis. MD may substitute for field duplicates (see below).
Method (Preparation) Blank (MB)	1 per 20 or SDG whichever is more frequent
Field Blank (FB)	Not applicable to archived sample analysis
Field Duplicate (FD) (historic)	1 per matrix per parameter per 20 samples, depending on availability. Matrix duplicates (MD) will be analyzed if insufficient archived duplicates are available.
Performance Evaluation (PE) Sample	1 every 3 to 6 months for each available matrix (non-aqueous and aqueous) for each laboratory analyzing PCBs.

12. Performance and System Audits and Frequency

Audits of the laboratories performing work in support of this program will be performed under the direction of the Quality Assurance Officer. At least one on-site audit will be performed during analysis at the PCB analytical facility. This is in addition to any laboratory facility audits which may be conducted prior to contract award.

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 bimonthly as the program proceeds. It is anticipated that a TAMS representative familiar with the historical analyses (e.g., Richard Bopp) will be present at the laboratory at the startup and during the packed column PCB analysis, and as necessary throughout that part of the project to provide direction and oversight.

The TAMS-contracted laboratories involved in analyses for this program will be audited under the direction of the QA Officer at the frequency listed above. Due to the special requirements associated with 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 to employ sound scientific judgment as necessary. The laboratory performing the PCB Aroclor analysis must adequately understand both the historical analytical method and the objective of the packed column analysis in order to generate comparable data to the original analysis.

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 lab and internal sample tracking
- Chain-of-Custody
- Sample storage

- Sample preparation/extraction and analysis including:
  - SOPs
  - Logbooks or bench sheets for all preparation procedures (including cleanups) of samples, calibration standards, QC standards/check samples, blanks
  - Logbooks or bench sheets 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 this SAP/QAPjP.
- QC samples documentation inclusive of items above for all blanks, calibrations, calibration verification check standards, matrix spike blanks, spikes, duplicates, spike duplicates, surrogates, control charts (were 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

13 Preventive Maintenance Procedures and Schedules

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 Specific Routine 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.

Analyses performed in this program will have a measure of precision in terms of matrix spike duplicates and field duplicates (where available); in some cases, analyses of matrix or laboratory duplicates may be used to compensate for missing field duplicates. See specific method SOPs (Appendix A) and Section 5 for further details.

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), the relative percent difference (RPD) between the two analyses 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)

For peak comparability of historic to current packed column PCB peak/Aroclor analyses (as described in Section 5.2.4.2), the relative RPD is calculated as follows:

$$\text{Relative RPD} = \frac{[(H_{hi}/H_{hmax}) - (H_{ci}/H_{cmax})]}{[(H_{hi}/H_{hmax}) + (H_{ci}/H_{cmax})]/2} \times 100\%$$

where: H_{hi} = Height of peak "i" in historic chromatogram

H_{hmax} = Height of maximum (largest) peak in historic chromatogram

H_{ci} = Height of peak "i" in current chromatogram (A-11 analysis)

H_{cmax} = Height of largest peak (as identified in historic analysis) in current chromatogram

Peak area or peak concentration may be substituted for peak height in the above equation for evaluation of the comparability criterion, provided that the basis used (peak height, peak area, or peak concentration) is used consistently throughout the program.

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.

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

or

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

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

14.2 Accuracy

The determination of accuracy of a measurement requires a knowledge of the true or accepted value for the signal being measured. Accuracy is assessed by calibration verification or matrix spike sample analyses, and analysis of other samples whose true value is known to the laboratory. In addition, analytical accuracy will be assessed by submission of performance evaluation (PE) samples to the laboratory (whose true value is unknown to the laboratory). 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. Surrogate recovery is also calculated for PCB congener analyses as an indicator of the accuracy of the method on a particular sample.

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

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 the required 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. Data are

reviewed in terms of project goals in order to determine if the data base is sufficient. Following data validation, the % completeness can be obtained as the following calculation:

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

It should be noted that a number of factors may result in obtaining less than 100% of the planned data. for the archived samples, these may include: an acceptable archived sample or extract was not available; packed column analysis did not meet comparability criteria; or analytical deficiencies (serious QC problems resulting in the data being unusable [rejected]). For the analysis of archived sediment core extracts or samples, the goal is to obtain at least three valid PCB congener analyses (out of a possible four or five) for each core. For the water column samples, the minimum completeness goal is 50%.

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 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. For routine corrective actions and maintenance, the actions taken will be noted in laboratory notebooks or bench sheets. For serious corrective actions, a memorandum will be issued to the QA Officer (QAO) 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.

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;
- 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 (TAMS/Gradient or USEPA).

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 action 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, laboratory QC Director, or the QAO or QA staff. 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.

Documentation of long term corrective actions will also be forwarded to the project QAO (Dr. Dallas Wait). This permanent record will aid the QC Director in follow-up action and this log will be reviewed by the QAO during project 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 (QAO) will issue reports pertaining to all quality assurance assessments and issues which occur during the project. The reports will include, as appropriate, the results of the 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 laboratory audits will be submitted to the TAMS project manager within 14 days following the audit. Serious deficiencies will be reported within one day of the audit with corrective actions identified. Followup reports confirming the implementation of corrective action, including evidence that the quality problem has been eliminated, will be issued as appropriate by the QAO.

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18 List of Abbreviations

CCB Continuing Calibration Blank

CCV Continuing Calibration Verification (Continuing Calibration Check) Sample

CLP Contract Laboratory Program

COC Chain-of-Custody

CV Coefficient of Variation

DCR Document Control Room

ESAT Environmental Services Assistance Team (EPA Contractor)

FB Field Blank

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

MSB Matrix Spike Blank

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 (also abbreviated QAPP)

QC Quality Control

QCC Quality Control Coordinator

RAS Routine Analytical Services

RPD Relative Percent Difference

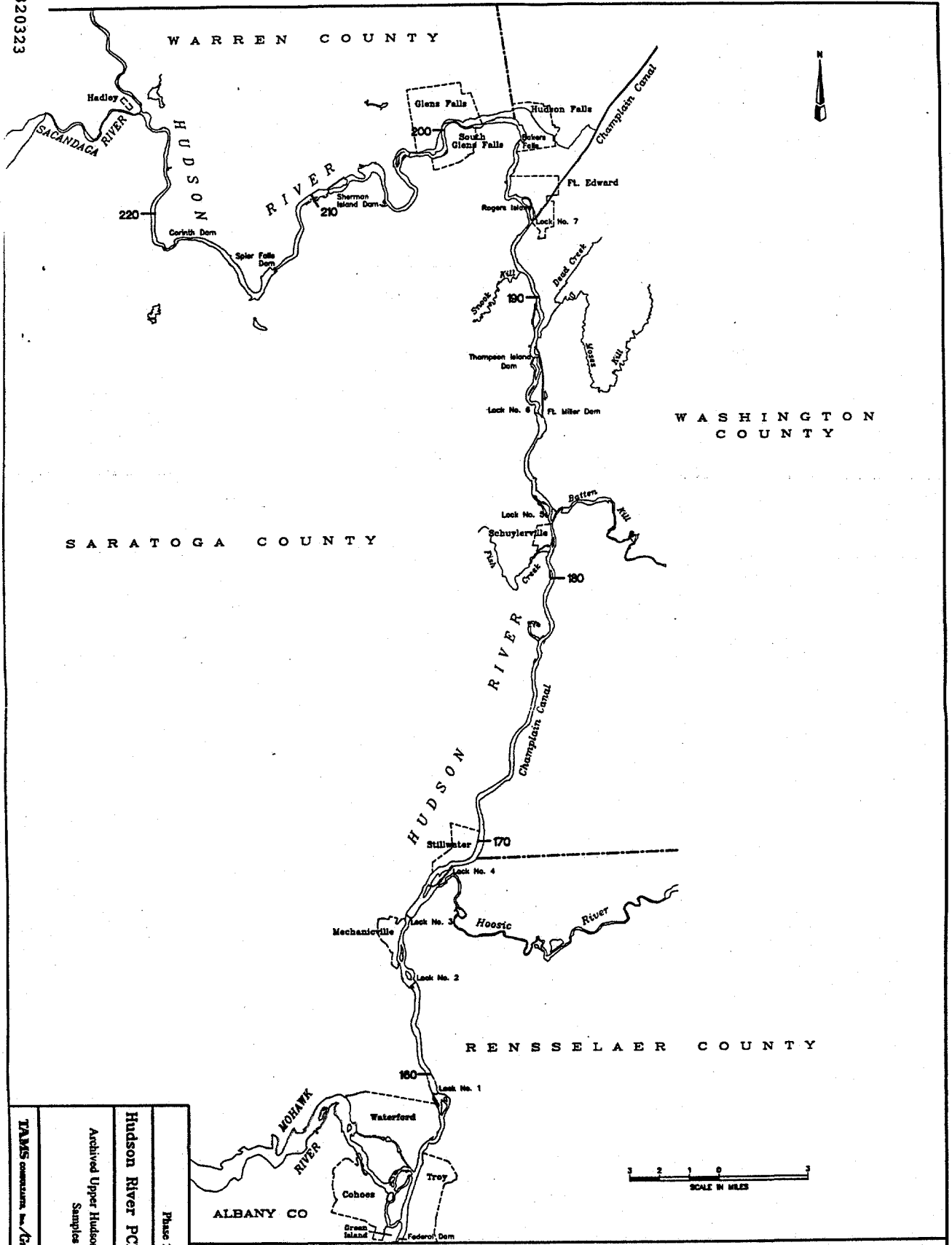
RRT Relative Retention Time

RSCC Regional Sample Control Center

RSD Relative Standard Deviation

SAP	Sampling and Analysis Plan
s	Standard Deviation (also abbreviated as SD)
SAS	Special Analytical Services
SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
TCL	Target Compound List (Organics)

320323



Legend

Phase 2B Investigation

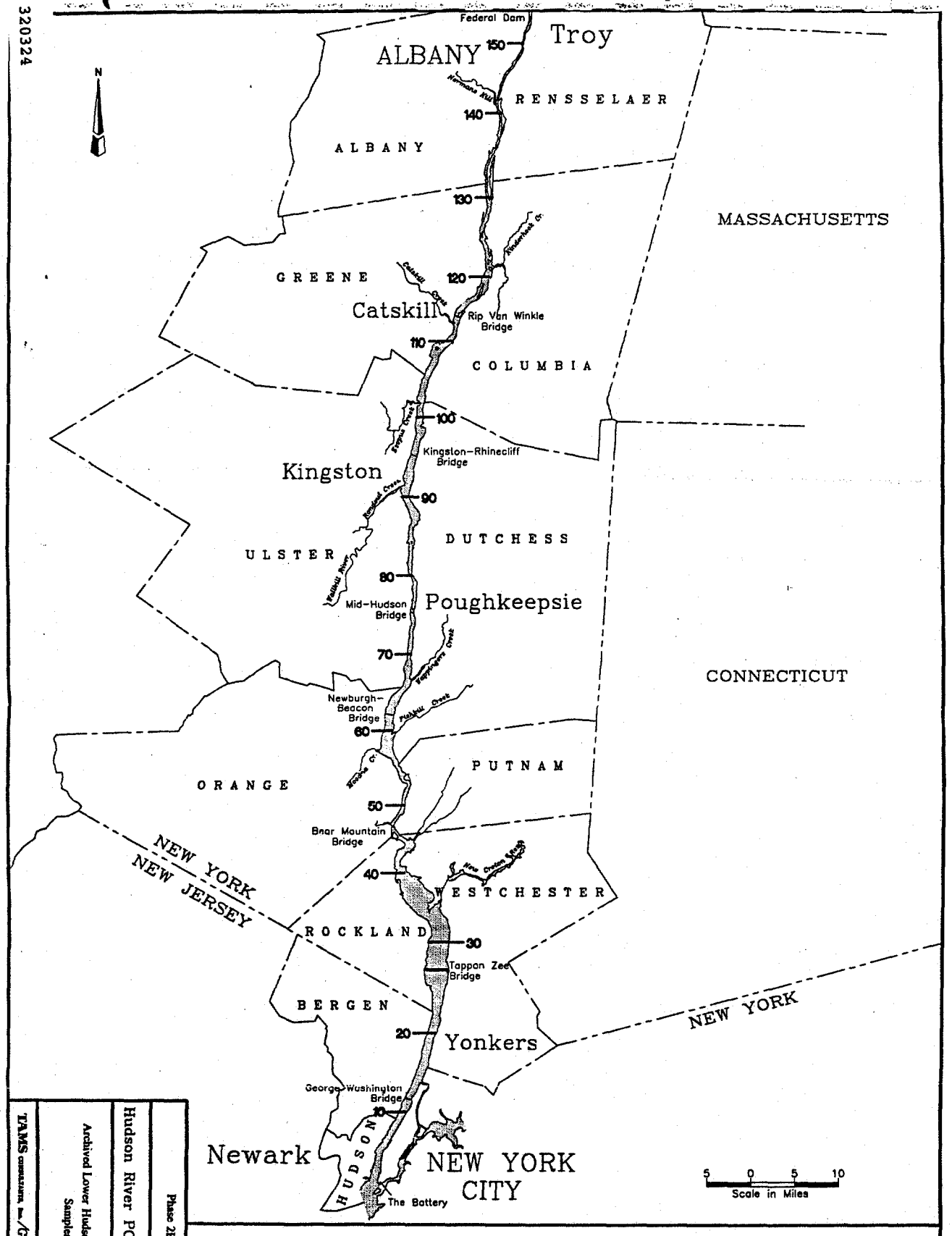
Hudson River PCB Reassessment RI/FS

Archived Upper Hudson Sediment and Water Column Samples to be Analyzed

TAMS consultants, Inc./Gradient Corporation

Figure 3-1

320324



Legend

Phase 2B Investigation

Hudson River PCB Reassessment RI/FS

Archived Lower Hudson Sediment and Water Column Samples to be Analyzed

TAMS consultants, Inc./Gradient Corporation

Figure 3-2

A

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/permanganate cleanup), and the method of Dr. Richard Bopp (1979), 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/ion trap detector (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 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. The use of phthalate-free gloves is recommended when handling samples or extracts, or glassware which may contact samples or extracts. Extensive 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 throughout this procedure, except where otherwise indicated. 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(s) - Pesticide quality or equivalent; typically at least 85% n-hexane.

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 the 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 this 2-ml standard to silica gel column and elute column with 30-ml hexane. Collect the 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) or BZ #192.

5.8.2 Prepare the surrogate standard spiking solution at a concentration of 0.2 μg/1.00 ml of each of the surrogate spike 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 Mix the sediment sample thoroughly, especially samples which have been field composited. Discard foreign objects such as sticks, leaves, and rocks.

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. 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 - 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 the silica gel. Mix slurry to remove air bubbles. Cover the 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 a 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 the methylene chloride. DO NOT LET SODIUM SULFATE BECOME EXPOSED 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 the stopcock to let methylene chloride drain out. Rinse the walls of column with methylene chloride so all of the silica get will fall into the restricted part of the column. Tap the column to settle the silica gel. Mark the top of silica gel with a marker and continue tapping until silica gel is settled. Discard the bulk of the methylene chloride to 2-cm above the 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 the top of the 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 the K-D apparatus. Add 30-ml hexane to the column and drain to the top of the sodium sulfate. Concentrate the 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.

$$\textit{Volume (ml)} = \textit{(initial weight (g) - final weight (g))} \times \frac{1}{\textit{0.66 (density of hexane g/ml)}}$$

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 must 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 The specified surrogate standards must be added to all samples, matrix spike samples, blanks, and standards.

8.3 A method blank must 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 must be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 14-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 quantitation.

8.5 A Matrix Spike Blank must be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 14-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 PCB congeners at a concentration appropriate to the anticipated sample concentrations (see Table 1).

8.7 For the archived sample analysis program, it is not expected that field duplicate samples will be available. Therefore, the analytical laboratory shall prepare and analyze one matrix (analytical) duplicate to assess precision at a minimum frequency of one per 20 analyses for the GC/ECD congener analysis of archived extracts or samples.

9.0 References

9.1 USEPA "Test Methods for Evaluating Solid Waste" - Third Edition (SW-846) Revision 1, July 1992. Methods 3500A, 3540A, 3630A, and 3660A.

9.2 USEPA "Test Methods for Evaluating Solid Waste" (SW-846), Proposed Update II, November 1992. Method 3665; also, proposed revision 3630B.

9.3 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-Trichlorobiphenyl	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-10
STANDARD OPERATING PROCEDURE

EXTRACTION AND CLEANUP OF DRIED, ARCHIVED SEDIMENT SAMPLES FOR PACKED COLUMN ANALYSIS OF POLYCHLORINATED BIPHENYLS

ABSTRACT

1.0 Scope and Application

The purpose of this procedure is to repeat polychlorinated biphenyl (PCB) analytical work which was performed during the 1970s and 1980s. While various parts of these procedures may have been improved during the past two decades, it is not the intent of this project to employ state of the art techniques as they exist today.

Sediment samples were collected, air dried, ground using mortar and pestle, and stored (archived) in air-tight aluminum cans. Samples are Soxhlet extracted with 60:40 acetone/hexane and the extract is concentrated in a Kuderna-Danish (K-D) apparatus. Initial separation of PCBs from more polar extractables is effected by column chromatography on alumina. Removal of elemental sulfur from the samples is effected by treatment with activated copper powder. The sample is again K-D concentrated and column chromatographed on silica. The extract is then analyzed by on a packed column gas chromatograph (GC) equipped with an electron capture detector (ECD).

2.0 Summary of Method

2.1 A portion of the dried (archived) sediment sample is reconstituted with water, placed in an extraction thimble, and extracted with a 60:40 mixture of acetone and hexane in a soxhlet extractor.

2.2 The extract is then dried with anhydrous sodium sulfate and concentrated in a K-D apparatus to 2 to 4 ml.

2.3 Alumina column chromatography, sulfur removal by copper, and silica column chromatography are then employed to clean the extract.

2.4 The sample is then reconcentrated to a final calibrated volume of approximately 2 ml.

2.5 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 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 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. The use of phthalate-free gloves is recommended when handling samples or extracts, or glassware which may contact samples or extracts. 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. The glassware is then scrubbed with a brush, hot tap water and Alconox, and rinsed with warm tap water. It is then rinsed with or soaked in chromic acid solution and rinsed with tap water. If the tap water does not sheet perfectly over the inside of the glass, the chromic acid washing or soaking must be repeated. After the tap water rinse, the glassware is rinsed with reagent grade water and acetone, and placed in an 80° C oven to dry. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent.

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. A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation Flask - 250 ml. Attach to concentrator tube with springs.

4.2.3 Snyder column - Three-ball macro.

4.2.4 Snyder column - Two-ball micro.

4.2.5 Concentrator tube - 25 ml, graduated.

4.2.6 Snyder column - 3 chamber.

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 - Fired overnight in a muffle furnace at 375°C.

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.

4.13 Long stemmed powder funnel.

4.14 Glass wool - Soxhlet extracted for at least two hours with 60:40 (v/v) acetone/hexane solvent mixture.

4.15 Apparatus for Alumina Column cleanup procedure:

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

4.15.2 250-ml beaker.

4.15.3 Long glass rod.

4.15.4 Glass wool - Rinsed with methylene chloride.

4.16 Erlenmeyer Flask (125 cc) - calibrated volume at approximately 50 ml.

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 Preparation of Silica

5.6.1 Silica gel (SiO_2) (Bio-Rad 100 to 225 mesh) is bulk dried overnight at 130° C and stored in a glass stoppered Erlenmeyer flask in a drying cabinet (good indefinitely).

5.6.2 3.20 gm ($\pm$ 0.01 gm) of SiO_2 from step 5.6.1 is weighed out into a glass scintillation vial and dried at least 4 hours at 130° C.

5.6.3 The SiO_2 is cooled in a drying cabinet and deactivated with 80 ul (2.44% w/w) of reagent grade water.

5.6.4 The vial is closed using a foil lined screw cap and an added Teflon liner and shaken at least 5 minutes to thoroughly disperse the water.

5.6.5 When no clumps of wet SiO_2 remain either in the vial or attached to the wall, the silica is allowed to stand and equilibrate with the water for at least three hours prior to use.

5.6.7 At this point, the silica can be stored with the cap on in a drying cabinet, but should be used within a few days.

5.6.8 The exact percent water on the silica used in the column must be determined by running a standard of Aroclor 1242 and the silica gel calibration mix to optimize the separation of the 4,4'-DDE and PCB fraction from the 4,4'-DDT (pesticide) fraction. Each lot of silica must be standardized

5.7 Preparation of Activated Copper

5.7.1 Copper powder, electrolytic dust (Fisher Scientific or equivalent) is added to a 60 ml funnel with a coarse glass frit. About 5 gm of copper per sample is normally allowed.

5.7.2 Concentrated hydrochloric acid (HCl) is added (approx. 30 ml) and the mixture is stirred with a glass rod. The HCl is filtered off under suction from an aspirator.

5.7.3 Repeat the HCl washing until the filtrate runs clear (about 3 times).

5.7.4 Wash with 30 ml reagent grade water (3 times), acetone (3 times) and hexane (3 times).

5.7.5 The funnel with the clean bright copper powder is connected to a tank of nitrogen equipped with a calcium sulfate drying trap. The copper can be stored for up to a day without reactivating with HCl if a minimum flow of nitrogen is maintained through the frit to prevent oxidation of the copper surface.

5.8 Preparation of Alumina

5.8.1 Aluminum oxide, Al_2O_3 (AG7 Bio-Rad 200 mesh, or equivalent) is bulk dried overnight at 250°C and stored in a glass stoppered Erlenmeyer flask in a drying cabinet (good indefinitely).

5.8.2 6.00 gm ($\pm$ 0.01 gm) of Al_2O_3 from step 5.8.1 is weighed out into a glass scintillation vial and activated for at least 4 hours in a 250° C oven.

5.8.3 The Al_2O_3 is cooled in a drying cabinet and deactivated with 385 microliters (ul) (6% w/w) of reagent grade water added by finnpipette.

5.8.4 The vial is closed using a foil lines screw cap and an added Teflon liner and shaken for at least 5 minutes to thoroughly disperse the water.

5.8.5 When no clumps of wet Al_2O_3 remain either in the vial or attached to the wall, the alumina is allowed to stand and equilibrate with the water for at least three hours prior to use.

5.8.6 At this point the alumina can be stored with the cap on in a drying cabinet for up to one week.

5.9 PCB Surrogate Standard Spiking Solution

5.9.1 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), unless other surrogates are specified in the analytical procedure or project-specific plans.

5.9.2 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.

5.10 PCB Aroclor Matrix Standard Spiking Solutions

5.10.1 Prepare a matrix spike standard solution that contains Aroclor 1242 in acetone. Final concentrations in samples should be about 10 to 15 times the MDL (see Appendix A-11). 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.

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

5.11 Hydrochloric Acid (concentrated)

6.0 Sample Preservation and Handling

6.1 Samples will be hand-delivered or delivered by commercial overnight delivery service to the laboratory.

6.2 Archived extracts must be protected from light and stored at 4° C ($\pm$2°) or kept frozen. Sediment and filter (suspened matter) samples must be stored securely but do not require refrigeration until opened.

6.3 Samples must be extracted within 5 days of removal from their containers. Opened containers must be kept refrigerated until they are resealed. Extracts must be analyzed within 40 days of VTSR, unless specified otherwise in the site-specific SAP/QAPjP.

7.0 Procedure

7.1 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 7.3).

7.2 Weigh out a 2.0 g dry sediment sample into a tared 50-ml beaker. Add 0.5 g or 0.5 ml (i.e., 25% by weight) of reagent grade water; the weight or volume of water added must be measured and recorded. Mix thoroughly with a stirring rod for approximately 3 minutes. Calculate the dry weight of the sample as follows:

$$\%\ dry\ weight = (g\ dry\ sediment/[g\ dry\ sediment + g\ water\ added]) \times 100\%$$

For the purpose of this calculation, it may be assumed that 1.0 ml water is equal to 1.0 gm of water.

7.3 Place a pre-extracted glass fiber thimble into a 50 ml beaker. Add approximately 5 g of Ottawa sand to the bottom of the thimble and tare on a top loading balance. (The sand will aid drainage of the thimble during the soxhlet extraction.) Transfer 2 g (± 0.001 g) of wetted sediment to the thimble and top with another 5 g portion of sand.

Determine the weight loss on ignition of the sample by first drying an approximately 0.5 g aliquot overnight at 105°C. Allow to cool in a desiccator before weighing and record weight to 0.001g. Then place the tared crucible or aluminum weighing dish with the dry sample into a muffle furnace at 375°C for a minimum of 16 hours. Allow to cool in a desiccator before weighing and record weight to 0.001 g.

% weight loss on ignition = [(g dry sample - g ignited sample)/g dry sample] x 100%

7.4 Mix the contents of the thimble with a stirring rod being careful not to lose any sediment. The extraction thimble must drain freely for the duration of the extraction period. Add 1.0 ml of surrogate standard spiking solution onto the sample. For the sample in each analytical batch selected for spiking, add 1.0 ml of matrix spike standard solution. The surrogate and matrix spiking procedures must be witnessed by another analyst, and verified on the extraction log.

7.5 Place 125 ml 60:40 (v/v) of acetone/hexane solvent mixture into a 250-ml round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for approximately 16 hours at 4 - 6 cycles/hr.

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

7.7 An extra long stemmed powder funnel is fitted with a slug of solvent-rinsed glass wool topped with 3-4 cm of sodium sulfate, then washed with 15 ml of methylene chloride followed by 15 ml of hexane.

7.8 The extract is then filtered through the drying funnel into a 500 ml Kuderna-Danish (K-D) evaporation flask and rinsed with 15 ml of hexane.

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

7.10 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 - 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.

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

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

7.13 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 at 4°C ($\pm$ 2°C).

7.14 Alumina Column Cleanup.

7.14.1 Alumina Column Preparation - Weigh 3 gm of deactivated alumina in a 50-ml beaker and add enough methylene chloride to cover alumina. Mix slurry to remove air bubbles. Cover beaker with aluminum foil until ready for use. Do not let methylene chloride evaporate to expose alumina. 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 1 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 EXPOSED TO AIR.

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

7.14.3 Add 1 cm granular sodium sulfate to the top of the alumina and rinse the column with about 50 ml of methylene chloride. Drain the 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 alumina column (exposed to air) dry; then rinse the sides of column with hexane and drain to top of granular sodium sulfate. Add 50 ml of hexane to the column and drain so hexane layer is just above the granular sodium sulfate.

7.14.4 Extract cleanup - Transfer the extract to the sorbent bed and drain to the top of the sodium sulfate. Drain the extract to the top of the sodium sulfate. A 0.5 ml hexane rinse of the K-D bottom or extract vial is added to the column and allowed to run to the top of the sodium sulfate 3 times. Start collecting the eluent at this time into a flask. Add 50 ml of hexane to column and drain to the top of the sodium sulfate.

7.15 The alumina column eluate must now be further cleaned with copper as described below.

7.16 Copper Cleanup.

7.16.1 Approximately 1 g of freshly prepared copper powder is added to the eluate and the flask is swirled briefly. If all the copper blackens (indicating sulfide formation), additional copper is added until the bright copper color persists. The flask is them swirled to permit maximum contact of the eluate with the copper. The total mixing time should not exceed 5 minutes.

7.16.2 The sample is immediately transferred to a K-D apparatus through a funnel equipped with a solvent rinsed glass wool plug to filter out the copper. The flask is then rinsed with 5 ml of hexane and transferred to the K-D apparatus through the funnel three times.

7.16.3 Add boiling chips to the K-D apparatus and concentrate extract to approximately 2 ml.

7.17 The concentrated copper cleaned extract must now be further cleaned on a silica gel 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.

7.18 Silica Gel Cleanup.

7.18.1 Silica Gel Column Preparation - Weigh 3 gm of deactivated silica gel in a 50-ml beaker and add enough methylene chloride to cover the silica gel. Mix slurry to remove air bubbles. Cover the 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 the 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 a 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 the methylene chloride. DO NOT LET SODIUM SULFATE BECOME EXPOSED TO AIR.

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

7.18.3 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 the sides of the column with hexane and drain to the top of the granular sodium sulfate. Add 25

ml of hexane to the column and drain so the hexane layer is just above the granular sodium sulfate.

7.18.4 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 the top of the sodium sulfate. Start collecting the eluent at this time into K-D apparatus. Add 25 ml hexane to the column and drain to the top of the sodium sulfate. Concentrate the extract to approximately 1.0 ml.

7.19 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.

7.20 Remove the Snyder column and 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. The 10-ml K-D tube must be wiped dry so that the final extract volume is accurate. 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.

$$\textit{Volume (ml)} = \textit{(initial weight (g) - final weight (g))} \times \frac{1}{\textit{0.66 (density of hexane g/ml)}}$$

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

7.21 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for the Aroclors present in calibration standards. 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 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 14-day calendar period during which samples are received, whichever is more frequent. The spiked Aroclor is used to monitor sample matrix effects which could interfere with the accuracy or precision of the PCB quantitation.

8.5 A Matrix Spike Blank should be extracted for each 20 samples in a Sample Delivery Group of similar matrix or each 14-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.

9.0 References

The procedure described in this SOP is adapted from the following source:

Bopp, R.F., The Geochemistry of Polychlorinated Biphenyls in the Hudson River. Ph.D. Dissertation, Columbia University, 1979.

APPENDIX A-11
STANDARD OPERATING PROCEDURE

PACKED COLUMN GAS CHROMATOGRAPHY ANALYSIS OF POLYCHLORINATED BIPHENYLS USING ELECTRON CAPTURE DETECTION

1.0 Scope and Application

The purpose of this procedure is to repeat polychlorinated biphenyl (PCB) analytical work which was performed during the 1970s and 1980s. While various parts of this procedure may have been improved during the past two decades, it is not the intent of this project to necessarily employ state of the art techniques as they exist today.

In general, the different components of the procedure are presented much as they were used during the earlier analyses. Gas chromatography was originally performed on a Varian Model 3700 instrument equipped with dual ^{63}Ni electron capture detectors operating in the pulsed mode. While the aim of this project is to repeat the analyses under conditions as close as possible to those presented herein, it is understood that some conditions may not be possible to reproduce and some equipment/supplies may not be available. Use of a Varian gas chromatograph is not mandated due to the restrictions it would place on carrying out this project. Therefore, exact chromatographic conditions (such as gas flow) may have to be modified in order to achieve adequate method performance. Modifications from the procedure presented herein must be minimized, and any such modifications must be documented and approved prior to their implementation.

Quantitation will be as total PCBs derived from the sum of the individual PCB peak concentrations, based on standards of PCB Aroclors 1242, 1254, and 1260, and decachlorobiphenyl. A single standard each of Aroclor 1221 and 1016 will be run at the beginning of the program to enhance data comparability for other purposes.

2.0 Summary of Method

2.1 Hexane extracts are analyzed for PCBs resolved to 25 peaks, which include monochlorobiphenyls to decachlorobiphenyl, using a packed column gas chromatograph with an electron capture detector (GC/ECD). PCB peaks are identified based on retention times relative to Aroclor standards. Prior to sample analysis, the laboratory is

required to use Aroclor standards for 1242, 1254, 1260 and decachlorobiphenyl (DCB) to determine the retention time order of the resolvable peaks. The laboratory will also determine the method detection limit for each of the 25 resolvable PCB peaks. A three-point calibration using Aroclor 1242, Aroclor 1254, and Aroclor 1260/DCB standards will be performed for quantitation. Instrument stability will be verified every 12 hours with mid-level standards.

2.2 Method interferences may be caused by septum bleed, contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts 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 - alumina column cleanup, silica gel, and sulfur cleanup (see appropriate Appendix A-10 for extraction and cleanup protocols) - are the minimum sample preparation techniques which will be employed. These cleanups will be performed only on samples (i.e., dried sediment and filters); extracts being reanalyzed will not be subject to any further cleanup.

3.0 Apparatus and Materials

3.1 Gas chromatograph - A gas chromatograph analytical system with a packed column, an electron capture detector, packed column or on-column injection, and required accessories including syringes, gases, strip-chart recorder with recording integrator, and auto-sampler, or equivalent.

3.2 Packed Column - 6 ft by 2 mm i.d. glass column packed with 4% SE-30/6% OV-210 on 80-100 mesh Chromosorb W HP, or equivalent. A 6 ft, 1/4 inch o.d. glass column packed with 3% SE-30 on 80/100 mesh Gas Chrom Q has been reported to provide similar chromatography.

3.3 A data system capable of handling the output from the chromatograph, a minimum of 40 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.

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.)

4.2 Stock Standard Solutions. Stock standards of each of the Aroclor mixtures (1242; 1254; and 1260/DCB). Stock standard solutions may be obtained from a commercial vendor, but the purity and concentration must be documentable. 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. Documentation of the quality of the standards (e.g., % purity) by the manufacturer or vendor must be supplied prior to the initiation of the work.

4.3 Primary Dilution Standard Solutions. Individual stock standards are combined to make intermediate stock solutions called the Primary Dilution Standard Solutions.

4.4 Calibration Standard Solutions. Calibration standards are prepared for Aroclor type (i.e., 1242, 1254, and 1260/DCB) by diluting Primary Dilution Standard Solutions (section 4.3) with hexane. Three concentration levels are prepared such that the lowest calibration standard for each Aroclor contains that Aroclor at a concentration roughly 5 times the MDL for that Aroclor. The highest standard should contain the specific Aroclor at 16 times the lowest calibration standard and the mid-level standard at approximately four times the concentration of the lowest standard. A surrogate (octachloronaphthalene or approved substitute) will be spiked into each standard and extract. Three different concentration levels of surrogate compounds will be used in the intitial calibration to assess linearity. 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.

A single mid-level of standard of Aroclor 1016 in hexane and a separate mid-level standard of Aroclor 1221 in hexane shall also be prepared. The mid-level standard for these Aroclors should be at the same concentration as the mid-level Aroclor 1242 standard.

4.5 Working standards must be changed monthly due to changes in concentration resulting from evaporation during use. Working standards must be changed more frequently if necessary.

5.0 Calibration

5.1 Initial calibration

Aroclor 1242, 1254, and 1260/DCB standards will be analyzed at three concentration levels to establish the linear response range on each instrument.

5.1.1 The initial calibration sequence is as follows:

1. Instrument Blank
2. Aroclor 1242 Calibration Standard 1 (ICALA1)
3. Aroclor 1242 Calibration Standard 2 (ICALA2) (= OCALA)
4. Aroclor 1242 Calibration Standard 3 (ICALA3)
5. Aroclor 1254 Calibration Standard 1 (ICALB1)
6. Aroclor 1254 Calibration Standard 2 (ICALB2) (= OCALB)
7. Aroclor 1254 Calibration Standard 3 (ICALB3)
8. Aroclor 1260/Decachlorobiphenyl Standard 1 (ICALC1)
9. Aroclor 1260/Decachlorobiphenyl Standard 2 (ICALC2) (= OCALC)
10. Aroclor 1260/Decachlorobiphenyl Standard 3 (ICALC3)
11. Instrument Blank

The mid-level standards for Aroclor 1221 and Aroclor 1016 shall be analyzed once during the first analytical sequence; analysis of these standards after the first analysis of the Aroclor 1260/DCB standards is recommended.

5.1.2 Linearity

The linearity for nine of the Aroclor 1242 peaks and which are used for quantitation and surrogate compound(s) is assessed using the three point calibration. The linearity (%RSD) criteria apply to Peaks 2 through 10. The linearity of Peak 1 and the early peaks at RRT 11 and RRT 16 is to be calculated and reported (also based on the Aroclor 1242 calibration), but these peaks are not required to meet the linearity criteria. The linearity for Peaks 11 through 15 is

assessed with the Aroclor 1254 calibration standards. The linearity of Peaks 16 through 22 and DCB is assessed with the Aroclor 1260/DCB calibration standards. Example chromatograms of the Aroclor standards are shown on Figure 1 (Aroclor 1242), Figure 2 (Aroclor 1254), and Figure 3 (Aroclor 1260 and DCB); the peaks and their RRTs are listed on Table 2. The following quality control criteria must be met on each gas chromatography system used for analysis:

5.1.2.1 Calibration factors (CFs) are calculated from the appropriate standard (see Table 2) for each of the 25 resolvable peaks used for individual peak and total PCB quantitation.

$$CF_x = \frac{(A_x)}{(C_s)(V_i)(F_x)}$$

where:

CF_x = Calibration Factor for Peak "X"

A_x = Response of Aroclor peak "X" in the mid-level standard.

C_s = Concentration of Aroclor in the mid-range standard (ng/μl).

V_i = Volume of standard injected (μl).

F_x = Fraction (as a decimal) Peak "X" in Aroclor Standard (from Table 2)

5.1.2.2 The Percent Relative Standard Deviation (%RSD) is calculated from the calibration factors for each of the 25 resolvable peak from the three-point calibration. The %RSD may not exceed 20% for Peaks 2 through 22 and DCB. No criteria are specified for Peak 1 and RRT 11 and RRT 16, but the laboratory must calculate and report the %RSD for these peaks.

$$\%\ RSD = \frac{SD_x}{CF_x}$$

where:

SD_x = Standard Deviation of Peak X

CF_x = Calibration Factor for Peak X

5.1.3 Retention Time Criteria

Each peak used in the initial calibration curve must fall within the specified retention time windows using the mean retention time of the three calibration points. The retention time windows are ± 2.0% of the mean retention time for all peaks and surrogates.

5.1.4 Instrument blanks must not have any Aroclors or peaks detected at a concentration greater than one-half of the calibrated quantitation limit (CQL). One-half the CQL should be approximately 2.5 times the MDL. (See section 6 for determination of the MDL.)

5.1.5 PCB quantitation peaks

In order to provide comparability with previous data, the quantitation peaks used for calculation of PCB concentrations shall be as shown in Table 2. Identification of the peaks taken from Bopp (1979) and Bopp and Simpson (1981) is shown in the example Aroclor standard chromatograms included as Figures 1, 2, and 3 of this appendix. Peaks shall be quantitated as total PCBs using the same peaks as were used in the initial (historical) analysis. Quantitation shall be on an Aroclor basis only when the initial analysis was reported as a specific Aroclor. Quantitation of Aroclor 1242 is based on peaks 4, 6, and 8. It is not anticipated that quantitation as Aroclor 1254 or 1260 will be required.

5.1.6 Concentrations of Standards

The three-point calibration for Aroclors 1242, 1254, and 1260/DCB shall span a 16-fold concentration range (as a minimum). The low concentration standards (ICALA-1, ICALB-1, and ICALC-1) shall be at approximately 5 times the MDL. The suggested concentrations for the remaining calibration standards are at 4 times the low standard for the mid-range standard, and at 16 times the low standard for the high standard. The concentrations of the mid-level Aroclor 1221 and Aroclor 1016 standards shall be comparable to the concentrations of the Aroclor 1242 mid-range standards.

5.2 Continuing Calibration

The continuing calibration standard (OCALA, the Aroclor 1242 midpoint calibration standard) must be analyzed every 12 hours and must meet the following quality control criteria. If sample data show the presence of significant concentrations of peaks quantitated from the Aroclor 1254 and/or Aroclor 1260/DCB CFs, then inclusion of

OCALB and OCALC (as appropriate) as additional continuing calibration standards is recommended. 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 percent difference (%D) of the average calibration factor (CF) as determined by the initial calibration as compared to the calibration factor calculated from the OCAL standard for each Aroclor peak used for quantitation may not exceed ± 25%.

$$\%D = \frac{CF_o - CF_i}{CF_i}$$

where:

CF_i = initial calibration factor
CF_o = continuing calibration factor

5.2.2 The retention times of the Aroclor peaks used for quantitation must fall within the retention time windows discussed in Section 5.1.3.

6.0 Method Detection Limit (MDL) and Extraction Efficiency Determinations

Prior to receiving environmental samples, the laboratory must determine method detection limits for each of the 25 resolvable peaks individually, and also calculate the MDL for Aroclor 1242 (based on peaks 4, 6, and 8) for the extraction and clean-up of dry sediment samples (Appendix A-10). The determination of individual peak MDLs will be calculated based on the weight percent data in Table 2. The laboratory must also demonstrate that acceptable Aroclor extraction efficiencies can be obtained using the extraction and analysis procedures defined in this and the accompanying SOPs.

6.1 MDL Determination for Dry Sediment Samples

6.1.1 Prepare seven low level MDL standards for each Aroclor mixture by spiking 3 to 5 times the concentration of the required detection limit for each Aroclor into 2-gram samples of dried sediment (supplied to the laboratory). Optimum concentrations may be 1000 ppb for Aroclor 1242 (Peaks 1 and 3 will be at 3 times the detection limit goal; RRT 11 and RRT 16 may not be detectable); 400 ppb for Aroclor 1254 (Peak 11 will be at 3 times

the detection limit goal); and 300 ppb Aroclor 1260 (Peak 20 will be at the detection limit goal; Peaks 21 and possibly 22 may not be detectable) and 8 ppb DCB (4 times the detection limit goal) for the Aroclor 1260/DCB standard. Due to overlapping peaks in the Aroclor mixtures, these Aroclors may not be combined into one MDL set. Three Aroclor mixtures and MDL sets are required: Aroclor 1242; Aroclor 1254; and Aroclor 1260/DCB. A total of 21 analyses will be required to perform this MDL study.

6.1.2 Extract these low level Aroclor MDL standards according to the procedure in Appendix A-10 (Extraction and Cleanup of Dried, Archived Sediment Samples for Packed Column Analysis of Polychlorinated Biphenyls).

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

6.1.4 Calculate the standard deviation of the results for each peak 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 peak
x_i	=	Result for Peak (i)
x_i	=	Mean result for Peak (i)
N	=	7 (number of MDL standard results)

6.1.5 Calculate the MDL for each peak (RRT 11; RRT 16; Peaks 1 through 22; and DCB) as follows:

MDL = 3.14 x SD

6.1.6 Calculate the MDL for Aroclor 1242 in the same manner as described above (Section 6.1.5) for individual peaks. Aroclor quantitation is described in Section 8.2.

6.2 Extraction Efficiency Determinations

6.2.1 Extraction efficiency determinations will be evaluated on four dried sediment samples, which are supplied to the laboratory.

6.2.2 The laboratory must extract and analyze each sample according to this SOP and the accompanying extraction SOP (Appendix A-10).

6.2.3 The laboratory must save the extracted samples and then re-extract those samples using the same procedures as specified in 6.2.2.

6.2.4 Extraction efficiencies will be evaluated as the mass of Aroclor (or DCB) peak recovered in the first extraction divided by the sum of the masses of the same Aroclor (or DCB) peak recovered 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 Aroclor or DCB peak removed in first extraction
M_s	=	mass of Aroclor or DCB peak removed in second extraction

6.4.5 Extraction efficiencies must be calculated for all 25 resolvable PCB peaks (RRT 11; RRT 16; Peaks 1 through 22; and DCB) and for each of the four samples analyzed. Extraction efficiencies must be at least 95% for Peaks 2 through 22 and DCB. Due to the limitations of the historical method, there are no mandatory criteria for the early eluting peaks; however, the extraction efficiency for RRT 11, RRT 16, and Peak 1 should be at least 80%. If any extraction efficiency for any of Peaks 2 through 22 or DCB 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 Packed Column Analysis

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

7.2 After the analysis of each group of samples, analyze an instrument blank followed by the mid-level Aroclor 1242 standard (OCALA). If significant concentrations of peaks quantitated from Aroclor 1254 or 1260 standards are detected in the samples, then analysis of these mid-level standards (OCALB and OCALC) is recommended. The analytical sequence must end with an OCAL standard regardless of the number of samples analyzed.

7.3 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.

7.4 Paragraphs 7.6 and 7.7 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 7.8.1.

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 7.8.1.

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

7.5.1 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.

7.5.2 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.

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

7.6 The calibration factors calculated for the continuing calibration standards are compared to the mid-range calibration factors from the initial calibration (ICALA-2 for Aroclor 1242, and ICALB-2 and ICALC-2 for Aroclors 1254 and 1260/DCB) and a percent difference (%D) is calculated for each Aroclor or DCB peak used for quantitation. The %D may not exceed ± 25% for each Aroclor peak. The %D criteria for RRT 11, RRT 16, and Peak 1 are advisory and not mandatory.

7.7 The retention time shift of the surrogates and PCB peaks in any standard or sample must be less than ± 2.0% from the mean retention time determined from the initial calibration.

7.8 Inject the sample or standard extract using either the solvent-flush technique or an auto sampler (the injection technique must be consistent throughout an analytical sequence). 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.

7.8.1 The analytical sequence must be as follows:

1-11. Initial Calibration (see Section 5.1.1); the instrument blank (step 11) begins the first 12 hour analytical window
12. Samples
13. Instrument Blank (must be the first injection after 12 hours of sample analysis)
14. OCALA (0 hour, begins the second 12-hour analytical window). If OCALB and/or OCALC are also run, second 12-hour window begins with last OCAL in this sequence.
15. Samples
16. Instrument Blank (first injection after the second 12 hour sample analysis period)
17. Repeat the above sequence starting with OCAL (step 12 above)
18. Analytical sequence must end with the analyses of OCALA; laboratory may also run OCALB and OCALC at conclusion of analysis.

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

7.9 Evaluate the chromatograms according to the following guidance.

7.9.1 Aroclors are not detected in the sample when no Aroclor concentration, based on the response of the three Aroclor peaks, is greater the established MDL for that Aroclor. Report the value as not detected (qualified "U") at the CQL.

7.9.2 Aroclors are detected at an estimated concentration in the sample when the Aroclor concentration, based on the response of the three Aroclor peaks, is between the MDL and the CQL. Report the calculated concentration as an estimated value (qualified "*J*").

7.9.3 Quantitation as an Aroclor or Aroclors is to be performed only on samples for which data was previously reported as Aroclors, based on information provided to the laboratory.

7.9.4 The ECD response for any analytical component must fall within the initial calibration range. Sample extracts containing Aroclor quantitation peaks exceeding the highest Aroclor calibration standard will require dilution.

8.0 Quantitation and Calculations

8.1 For all samples, data will be reported as "Total PCBs". Total PCBs are defined as the sum of the concentrations of the individual peaks present in a sample. Individual PCB peaks (not Aroclors) will be quantified using the weight percent data shown on Table 2 (from Webb and McCall, 1973). These data shall be used by the laboratory to calculate a calibration factor for each peak. Based on the historical results of this method, there are a total of 25 possible resolvable (quantifiable) PCB peaks (22 numbered peaks, plus two un-numbered early eluting peaks; and DCB, which elutes after peak 22). DCB, if present, shall be quantitated separately, and not included in the total PCB calculation. The calibration factor for each peak is determined as specified in Section 5.1.2.1.

8.2 Data shall be reported on an Aroclor basis only for samples for which data was originally reported on that basis. Calculate the concentration of Aroclors in dry sediment samples using the following equation for external standards. Response can be measured by automated peak height or peak area measurements from an integrator.

$$\textit{Concentration of one Aroclor peak } C_x \textit{ (ug/kg)} = \frac{(A_x)(V_t)}{(CF_x)(V_i)(W_s)}$$

Where:

A_x	=	Response of Aroclor quantitation peak to be measured.
CF_x	=	Mid-level calibration factor of Peak X as determined in initial calibration.
V_t	=	Volume of total extract (μl); take into account any dilutions.
V_i	=	Volume of extract injected (μl).
W_s	=	Weight (dry) of sample extracted (g).

Concentration of Aroclor in sample (ug/kg) = Average of 3 individual peak concentrations as calculated above

8.3 Concentrations of Aroclors and PCB peaks will be calculated by using the mid-level calibration factors (i.e., from ICALA-2, ICALB-2, and ICALC-2) as determined in the initial calibration of each resolvable PCB peak. PCB peaks and Aroclors will be quantified by peak height or peak area using external calibration.

8.4 Report results in micrograms per kilogram (ug/kg) for dry sediment samples. Sediment sample data are reported on a dry weight basis.

9.0 Quality Control

9.1 Instrument Blanks

9.1.1 An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The instrument blank volume must be approximately equal to the sample volumes being processed.

9.1.2 Instrument blank analysis must be performed prior to and at the completion of initial calibration (as shown in Section 5.1.1) and after prior to each 12-hour analytical window (as shown in Section 7.8.1).

9.2 Method Blanks

9.2.1 A method blank is a volume of baked sodium sulfate carried through the entire analytical scheme (extraction, cleanup, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

9.2.2 Method blank analysis must be performed at a frequency of at least once for 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.

9.2.3 It is the Laboratory's responsibility to minimize 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.

9.2.4 For the purposes of this protocol, an acceptable laboratory method blank must contain no confirmed Aroclor or PCB peak detected above the lowest calibration standard (calibrated quantitation limit, CQL). 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. Re-extractions should be performed within the 5 days of validated time of sample receipt (VTSR), whenever possible. The Laboratory Manager, or his designee, must address problems and resolutions in a Case Narrative.

9.2.5 The Laboratory must report results of method blank analysis.

9.2.6 The Laboratory must report sample concentration data as uncorrected for blank contamination.

9.3 Surrogate Spike (SS)/Retention Time Marker Analysis

9.3.1 Each sample, standard, and blank extract will be spiked with a surrogate spiking compound before extraction, or spiked into archived extracts, in order to monitor retention time shift.

9.3.2 The surrogate spiking compound shall be octachloronaphthalene (OCN) unless this compound is determined to co-elute with PCB peaks in the packed column analysis. In this case, the laboratory shall develop an alternative spiking compound subject to TAMS/Gradient approval. The spiking compound is used to fortify each sample or extract analyzed, including blanks, standards, and QC samples.

9.3.3 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 is less than 10 percent, the laboratory must re-extract and re-analyze the sample. If the surrogate recovery is less than 10% on the re-extraction and reanalysis, the laboratory shall report both analyses and note an apparent matrix affect in the case narrative. If surrogate recoveries are 10% or greater in the second analysis, report only the re-extraction and reanalysis results. The re-extraction requirement is not applicable to archived samples for which the archived extracts are analyzed.

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

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

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

9.4.1 In order to evaluate the matrix effect of the sample upon the analytical methodology, an Aroclor 1242 matrix spiking solution is to be used for matrix spike and matrix spike duplicate analyses. The spiking solution concentration should be approximately equal to that of ICALA-2 or OCALA.

9.4.2 A matrix spike and matrix spike duplicate must be performed on a sample at least once for 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 (beginning with the receipt of the first sample in that Sample Delivery Group); whichever is most frequent.

9.4.3 The analytical protocols in the accompanying SOP for the extraction and cleanup of PCBs from dry sediments (Appendix A-10) specify the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. The method allows for dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples. Samples requiring dilutions and chosen as the matrix spike/matrix spike duplicate samples must be analyzed at the same dilution as the original unspiked sample.

9.4.4 The recovery of the matrix spike is calculated using the equation below. Advisory recovery limits for the matrix spiking compound are 60 to 150 percent.

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

Where:

SSR	=	Spike Sample Result
SR	=	Sample Result
SA	=	Spiked Added from Spiking Mix

Sample and Spike Sample Results are calculated on an Aroclor basis as described above in Section 8.2.

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

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

Where:

RPD	=	Relative Percent Difference
D_1	=	Matrix Spike Result (Corrected for sample value)
D_2	=	Matrix Spike Duplicate Result (Corrected for sample value)

9.5 Matrix Spike Blank (MSB)

9.5.1 A Matrix Spike Blank (MSB) is a volume of granular sodium sulfate that has been spiked with the Aroclor matrix spiking solution (see section 9.4.1) and subject to the entire extraction and analysis procedure. The MSB is used to assess the performance of the method.

9.5.2 A Matrix Spike Blank must be extracted and analyzed 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 (period beginning with the receipt of the first sample in that Sample Delivery Group), whichever is most frequent.

9.5.3 The Aroclor matrix spiking solution should be added to the blank so that the resultant concentration of Aroclor 1242 in the Matrix Spike Blank is approximately 10 to 15 times the established MDL.

9.5.4 The Matrix Spike Blank must be evaluated by determining whether the concentration of each Aroclor 1242 quantitation peak (measured as percent recovery) falls within the advisory recovery limits of 60 to 150 percent. If the recovery falls 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.

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

9.6 Aroclor Calibration and Quantitation QA/QC Requirements

Section 9.6 through 9.8 summarizes ongoing QC activities involved with Aroclor analysis that were detailed in Sections 9.1, 9.2, 9.3, 9.4, and 9.5, and describes the additional QA/QC procedures required during the analysis of Aroclors that are not covered in Sections 9.1, 9.2, 9.3, 9.4, and 9.5.

The Laboratory must perform the following:

- Instrument Blank analysis as per Section 9.1.

- Method Blank analysis as per Section 9.2.

- Surrogate spike of all standards, samples, blanks, matrix spikes, matrix spike duplicates, and matrix spike blanks as per Section 9.3.

- Matrix Spike/Matrix Spike duplicate analysis as per Section 9.4.

- Matrix Spike Blank as per Section 9.5.

9.7 Packed GC Column Analysis

9.7.1 Prepare the Calibration Standards at the three concentration levels described in Section 4.4. Perform the calibration as specified in Section 5.1.1).

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

- Analyze an initial calibration sequence as described in section 5.1.1 and calculate and record the mean retention time for the peaks quantitated against each Aroclor (as shown on Table 2) from the initial three-point calibration.

- The retention time windows are calculated from the mean initial calibration at $\pm$ 2.0%.

- The relative retention time shift for any peak (relative to the mean initial retention time) must be within $\pm$ 2.0%.

9.7.3 Establish the calibration factor for each peak from an acceptable three-point initial calibration as described in Section 5.

9.7.4 Calculate the %RSD for each peak and surrogate using all three calibration points. The %RSD for Peaks 2 through 22 and DCB must be less than 20% (see Section 5.1).

9.8 Sample Analysis

9.8.1 Samples are analyzed in the sequence specified in Section 7.8.1.

9.8.2 The retention time shift for the surrogate standard must be evaluated after the analysis of each sample. The retention time shift may not exceed ± 2.0% for the surrogate.

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

$$\%D = \frac{RT_s - RT_i}{RT_i}$$

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

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

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

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

10. References

The procedure described in this SOP has been derived from the following sources.

Bopp, R.F., 1979. The Geochemistry of Polychlorinated Biphenyls in the Hudson River. Ph.D. Dissertation, Columbia University, New York, N.Y.

Bopp, R.F., H.J. Simpson, C.R. Olsen, R.M. Trier, and N. Kostyk, 1981. Polychlorinated Biphenyls in the Sediments of the Tidal Hudson River, New York. *Environmental Science and Technology*, 15, pp 210-216.

Webb, Ronald G., and Ann C. McCall, 1973. Quantitative PCB Standards for Electron Capture Gas Chromatography, *Journal of Chromatographic Science*, 11, July 1973, pp. 366-373.

Table 1
GC Operating Conditions

Gas Chromatograph with packed column and packed or on-column injection port and electron capture detector.

Configuration

A six foot x 2 mm ID glass column packed with 4% SE-30/6% OV-210 on 80-100 mesh Chromosorb W HP (4000 theoretical plates), or equivalent, is connected to a electron capture detector. If columns are packed by the laboratory, the columns should be deactivated prior to packing with Sylon-CT (Supelco, Inc. or equivalent). Packing can be accomplished using gentle tapping and a small positive pressure of dry nitrogen to aid the filling of the column.

Conditions

Column Temperature	-	195°C (isothermal)
Column Conditioning	-	72 hours; consisting of 18 hours at 225°C at 10 ml/min and 54 hours at 210°C and 10 ml/min.
Injection Port Temperature	-	210°C
Detector Temperature	-	240°C
Injection Amount	-	1 ul to 4 ul
Carrier Gas	-	nitrogen at 30 ml/min

TABLE 2

Aroclor Standards and PCB Weight Percent Data for Quantitation of PCB Peaks

Peak Number	Relative Retention Time (RRT)	Aroclor Standard Used For Peak Quantitation	Fraction of Listed Peak As Percent Composition of Applicable Aroclor Standard
--	11	1242	1.1%
--	16	1242	2.9%
1	21	1242	11.3%
2	28	1242	11.0%
3	32	1242	6.1%
4	37	1242	11.5%
5	40	1242	11.1%
6	47	1242	8.8%
7	54	1242	6.8%
8	58	1242	5.6%
9	70	1242	10.3%
10	78 plus 84	1242	6.3%
11	98	1254	7.5%
12	104	1254	13.6%
13	125	1254	15.0%
14	146	1254	10.4%
15	174	1254	8.8%
16	203	1260	9.3%
17	232 plus 244	1260	9.8%
18	280	1260	11.0%
19	332	1260	4.2%
20	372	1260	4.0%
21	448	1260	0.6%
22	528	1260	1.5%
DCB	>528	DCB	100%

Peak Numbering system from Bopp (1979) and Bopp et al. (1981]).
Relative Retention Time and Weight Percent Data from Webb and McCall (1973).

Figure 1

Packed Column Chromatogram of Aroclor 1242

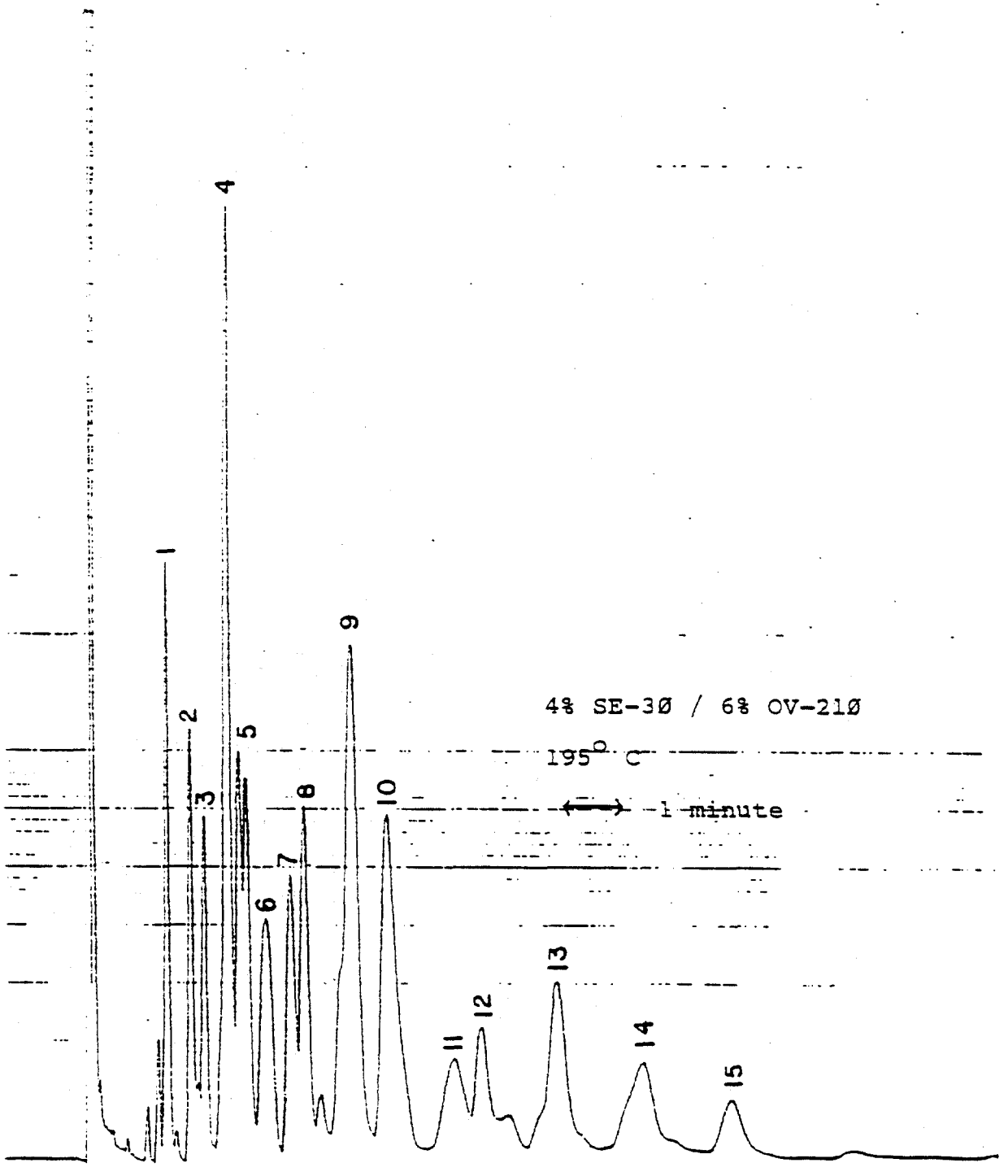


Figure 2
Packed Column Chromatogram of Aroclor 1254

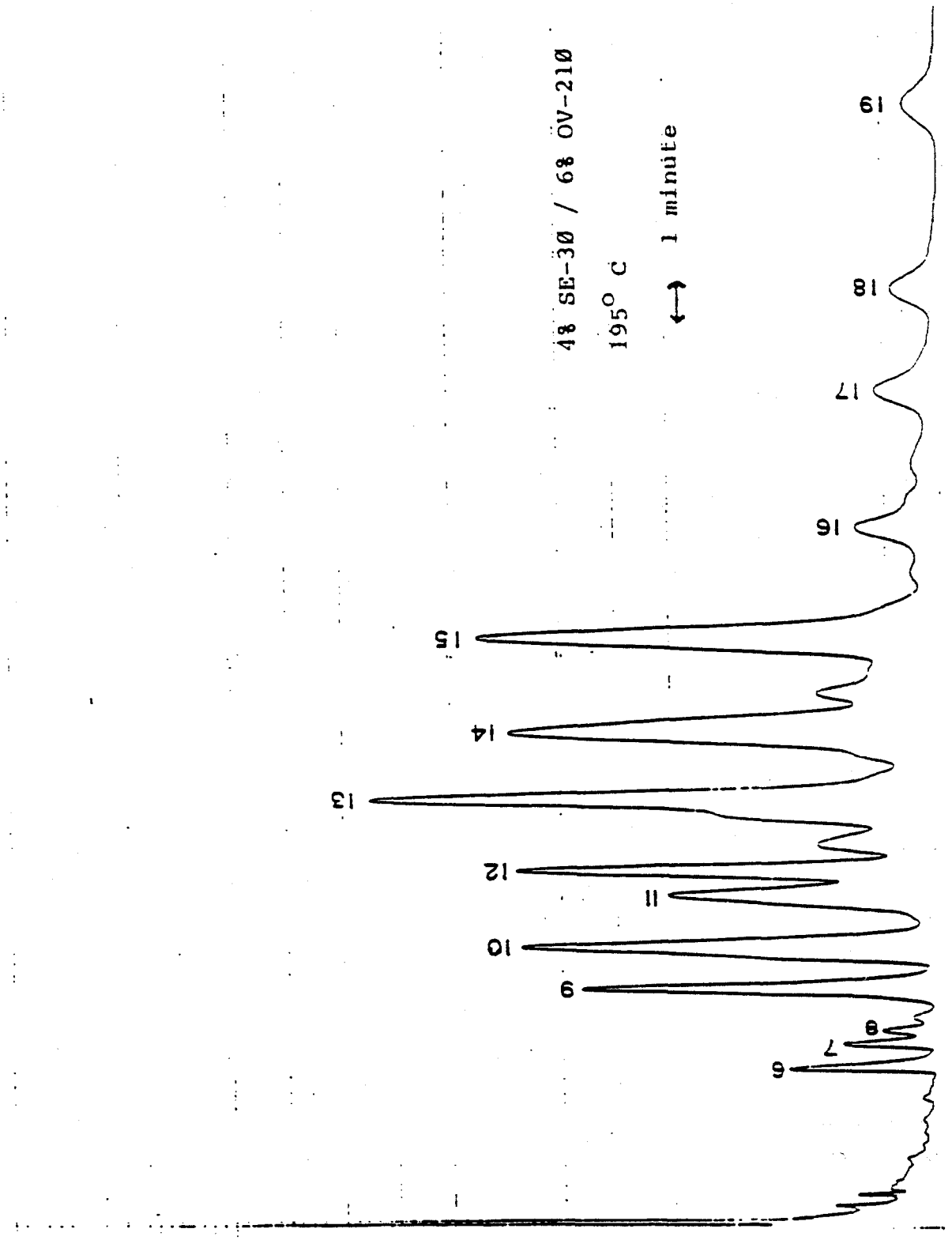
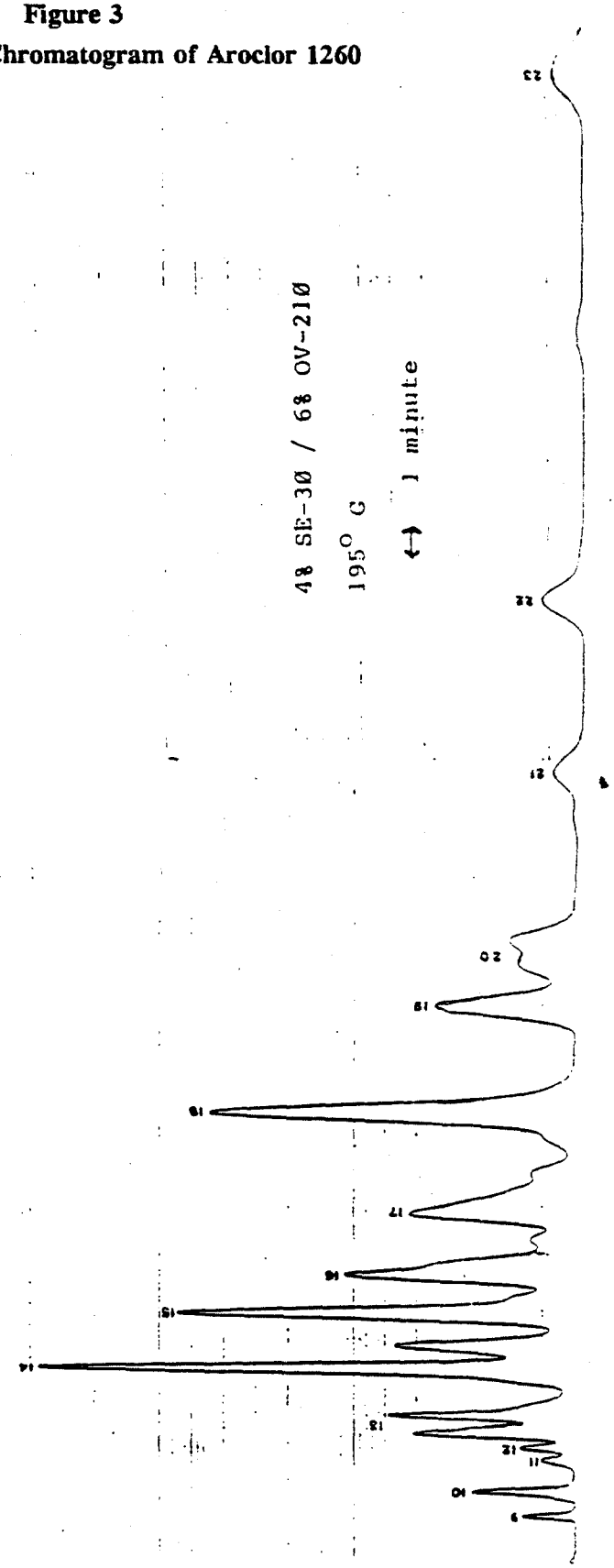


Figure 3
Packed Column Chromatogram of Aroclor 1260



C

APPENDIX C

FIELD PROCEDURES

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C-1
Sample Packaging and Shipping
TAMS SOP #61 (revised May 1994)

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SAMPLE PACKAGING AND SHIPPING STANDARD OPERATING PROCEDURE 61

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 samples taken from controlled or uncontrolled hazardous substance sites for analysis at CLP RAS or SAS laboratories (i.e., laboratories procured through the USEPA Sample Management Office). Paperwork, custody, and labeling requirements may vary for shipment of samples to laboratories contracted to TAMS; consult the project-specific plans for further guidance.

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.

"CLP" -- The USEPA Contract Laboratory Program, administered by the Sample Management Office.

"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.

"N.O.S." -- Not otherwise specified.

"N.O.I." -- Not otherwise indicated.

"ORM" -- Other regulated material.

RAS -- Routine Analytical Services (analyses for Target Compound List volatile or semivolatile organics, pesticides/PCBs, or Target Analyte List inorganics, as defined in the applicable CLP Statement of Work).

SAS -- Special Analytical Services; includes any analysis other than RAS for which laboratory services are procured through the USEPA Sample Management Office.

"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). 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 Sample Management Officer 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.

4. Picnic coolers or ice chests (preferably constructed of metal) capable of withstanding impact caused by a 1.8 m (5.9 foot) drop.

5. Tape - packing tape (strapping tape or duct tape) for securing the cooler; clear plastic tape for protecting labels.

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).

2. Appropriate pre-printed labels (see section 5.3.2.2 of this SOP)

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 (preferred) or plastic (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 chilling to 4° C is required.

Ice cubes are put in sealable polyethylene bags and placed around samples before the packing material covers the bottles. Sufficient ice must be added to bring the samples to 4° C, as well as to maintain that temperature during the anticipated interval between shipment and receipt at the laboratory.

The shipping container is filled completely with inert packing material (e.g., vermiculite) to minimize movement of the container's contents

within the container. When closed and ready for shipment, the cooler is secured with packing tape, covering the hinges, and drain (if present). Custody seals are placed on the cooler in at least two locations.

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. A custody seal is placed on each sample container. Chain-of-Custody forms and Traffic Reports are placed inside a large sealable plastic bag which is then taped to the inside of the top lid of the shipping container.

An address label (generally a pre-printed form provided by the carrier) is affixed to the top of the shipping container, along with proper labels (e.g., "This End Up"). It is strongly recommended that a second label with the destination of the cooler be affixed to one of the sides of the cooler. Custody seals are affixed to the lid in a manner that prevents opening of the shipping container without breaking the seals.

No USDOT marking or labeling is required for low concentration environmental samples.

5.3.1.3 Shipping Papers

No USDOT shipping papers are required for low concentration 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.

Samples should be shipped within 24 hours of collection unless otherwise specified in the site-specific project plans and approved by USEPA.

5.3.2 Medium Concentration Environmental Samples

The procedures to be used to pack, label, mark, and ship medium concentration 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. Fill the remaining empty space in the shipping container with an inert material such as vermiculite.

e. Mark and label the shipping container and complete shipping documents as described below. Secure the cooler with packing tape in the same manner as for low concentration environmental samples.

5.3.2.2 Marking and Labeling (see 49 CFR 172, subpart D [marking] and subpart E [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."). This is followed immediately by the hazard class (3 for flammable liquid N.O.S., and 4.1 for flammable solid N.O.S.); the UN identification number (UN 1993 for flammable liquid N.O.S. and UN 1325 for flammable solid N.O.S.), and the packaging group (abbreviated PG), either PG II or PG III (see below). Place the following labels on the outside of the cooler: "Cargo Aircraft Only" and "Flammable Liquid" (if not liquid, "Flammable Solid"). The total quantity of the material covered by the description follows the description (units of measure may be abbreviated). 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 "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.

Assignment of packaging group - unknown flammable liquids typically would be either PG II (medium hazard; for example, gasoline is PG II) or PG III (low hazard; for example, fuel oil is PG III). There some are flammable liquids N.O.S. which are PG I; however, such materials are not likely to be sampled by TAMS. Flammable solids N.O.S. are only PG II or III; contaminated soil samples are generally group III.

5.3.2.3 Shipping Papers (see 49 CFR 172, subpart C; especially 172.202)

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 inner container shall not exceed (1 to 5 kg net capacity) and the gross weight of each package (cooler) shall not exceed 30 kg (66 lbs).

Liquids: liquids in volume of (0.5 to 5.0 L per bottle) 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 may exceed the limit set for passenger aircraft. Coolers shall not exceed 30 kg (66 lbs) gross weight.

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.). The net volume of flammable solid may not exceed 50 kg for PG II and 100 kg for PG III; however, these limits are superseded by the 30 kg limit for "limited quantity" shipments.

   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 of flammable liquid N.O.S. for each cooler may not exceed 60 L for PG II or 220 L for PG III.

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 and Title
TAMS Telephone Number
Signature of Shipper

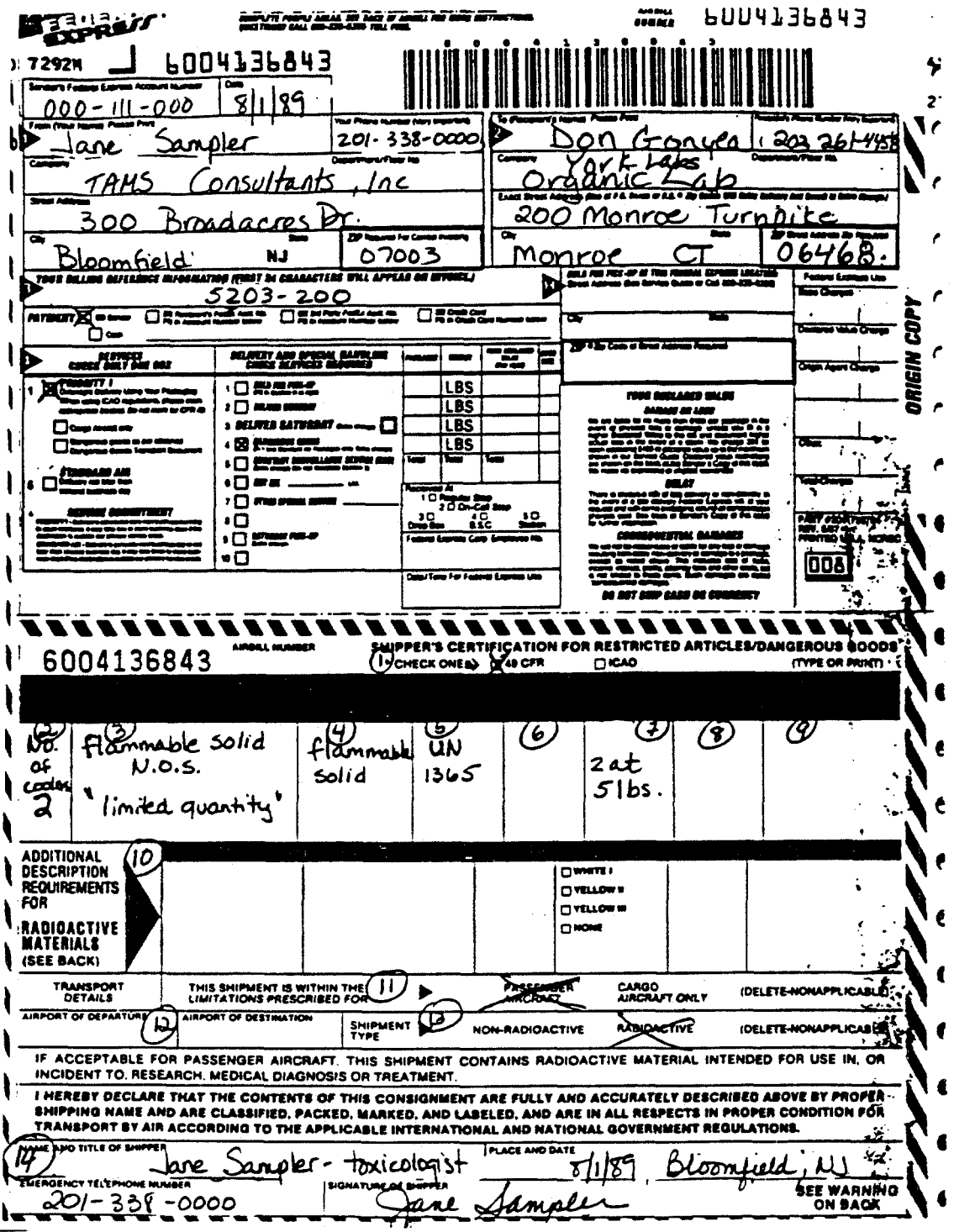
Note: Emergency response information may also be required for shipment of hazardous materials. Consult 49 CFR 172, subpart G (172.600 - 172.604) for details.

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.

SAMPLE PACKAGING AND SHIPPING STANDARD OPERATING PROCEDURE 61

FIGURE 61-1 - AIRBILL/SHIPPER'S CERTIFICATION FORM



FedEx EXPRESS

6004136843

7292M 6004136843

000-111-000 | 8/1/89

From: Jane Sampler | 201-338-0000

Company: TAMS Consultants, Inc

Street Address: 300 Broadacres Dr.

City: Bloomfield | State: NJ | ZIP: 07003

To: Don Gonyea | 203 261-4458

Company: York Lakes Organic Lab

Street Address: 200 Monroe Turnpike

City: Monroe | State: CT | ZIP: 06468.

YOUR BILLING REFERENCE INFORMATION: 5203-200

PAYMENT: Bill Sender

DELIVERY AND SPECIAL HANDLING: 4 Standard Air

LBS

ORIGIN COPY

6004136843 AIRBILL NUMBER

SHIPPER'S CERTIFICATION FOR RESTRICTED ARTICLES/DANGEROUS GOODS (1) CHECK ONE: X 49 CFR ☐ ICAO (TYPE OR PRINT)

(2) 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)

☐ WHITE I ☐ YELLOW II ☐ YELLOW III ☐ NONE

TRANSPORT DETAILS: THIS SHIPMENT IS WITHIN THE LIMITATIONS PRESCRIBED FOR (11) ▶ ~~PASSENGER AIRCRAFT~~ CARGO AIRCRAFT ONLY (DELETE-NONAPPLICABLE)

(12) AIRPORT OF DEPARTURE | AIRPORT OF DESTINATION | SHIPMENT TYPE (13) 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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