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Phase 2A Sampling and Analysis Plan/Quality Assurance Project Plan Hudson River PCB Reassessment RI/FS

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EPA Work Assignment No. 013-2N84 Revision 1 March 10, 1992

Prepared for EPA Region II Alternative Remedial Contracting Strategy (ARCS) for Hazardous Waste Remedial Services

EPA Contract No. 68-S9-2001

Prepared by TAMS Consultants, Inc. and Gradient Corporation Phase 2A Sampling and Analysis Plan/Quality Assurance Project Plan Hudson River PCB Reassessment RI/FS

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Hudson River PCB Reassessment RI/FS Phase 2 Revision 1 March 10, 1992

<u>Date</u>

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3 Project Description

In accordance with the Scope of Work for the Hudson River PCB Reassessment RI/FS (December, 1990), Phase 2 of the reassessment involves field sampling to further characterize and analyze site conditions at the Hudson River PCB Superfund site. As a result of Phase 1 evaluations, a two-part sampling effort is proposed, wherein an accelerated plan, described in the Phase 2A Sampling Plan, will sample and analyze water and sediment, and collect river geophysical data as soon as possible.

3.1 Background

3.1.1 Site Description

The Hudson River PCB Superfund site encompasses the Hudson River from Hudson Falls to the Battery in New York Harbor, 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 (Figure 3-1), is distinguished from the Lower Hudson stretch, from Federal Dam to the Battery (Figure 3-2). 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 suspended in water, from the Upper Hudson to the Lower Hudson. Figures 3-1 and 3-2 show the proposed high resolution coring locations for the upper and lower Hudson, respectively, and Figure 3-3 shows the proposed water quality monitoring stations.

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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 1.3 million pounds of PCBs were discharged between 1957 and 1975 from these two GE facilities. Discharges resulted from washing PCB-containing capacitors and minor spills.

The PCBs discharged to the river tended to adhere to sediments and subsequently accumulated downstream with the sediments as they settled in the impounded pool behind the former Fort Edward Dam. Because of its deteriorating condition, the dam was removed in 1973. During subsequent spring floods, PCB-contaminated sediments were scoured and released downstream. Exposed sediments from the former pool behind the dam, called the "remnant deposits," have been the subject of several remedial efforts.

Investigations at the site began after PCBs were reported in fish caught in the Upper and Lower Hudson in the early 1970's. In 1971, New York State Department of Environmental Conservation (NYSDEC) added PCBs to their statewide analyses of pesticide residues in fish, although no results were released publicly until 1975. After USEPA investigations in 1974 of PCB contamination in the Fort Edward area, NYSDEC intensified its PCB sampling program. In 1976, following the 1975-76 fish monitoring effort, NYSDEC banned all fishing in the Upper Hudson river from Albany north to Fort Edward due to the high levels of PCBs in fish. Commercial fishing for striped bass in the Lower Hudson was also closed at the same time. Both bans remain in effect.

USEPA under the NCP and CERCLA, or Superfund process performed a Feasibility Study in 1984 and issued a Record of Decision (ROD) for the site in 1984. The ROD called for: 1) an interim No Action alternative for river sediments; 2) in-place containment, capping, and monitoring of the remnant deposit sediments; and 3) a treatability study to evaluate the effectiveness of the

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Waterford Treatment Plant in removing PCBs from the river water. Since the signing of the ROD, the temporary fortification of the remnant deposits has been virtually completed. The Waterford treatability study concluded that the water supplied for drinking water meets all Federal and State standards (PCBs were below detectable levels).

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

The Phase 1 Report-Review Copy was issued in August 1991. A Phase 2A Sampling Plan-Review Copy was issued in September 1991. Additional Phase 2 sampling work will be issued in the Phase 2 Work Plan which will be prepared following the Phase 1 Report comment period.

3.2 Project Objectives

The Phase 2A analytical program for the Hudson River can be separated into four basic studies. Each study is designed to meet a specific project objective. The four basic studies and project objectives associated with each study are listed below.

Water Column Study - To investigate water column PCB levels, transport and sources.

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Water Column PCB Equilibration Study - To examine dissolved phase to suspended matter partitioning of PCB congeners.

Confirmatory Sampling Study - To examine river sediment for the purposes of interpreting geophysical data.

High Resolution Sediment Core Study - To examine long term trends in PCB transport, release and degradation via an examination of the sediment record.

Data calibration needs and required analyses for each study differ according to specific project objectives and media examined. In the following section of this QAPP, the specific objectives of each study are discussed along with the justification for individual analyses.

3.2.1 Water Column Study

The Phase 2A Water Column Study is intended to address several issues concerning riverine PCB contamination, including:

- the source or sources of PCBs at Ft. Edward which, on an annual basis, appears to be the only current source to the Upper Hudson, as suggested by the Phase 1 Report;
- the nature of the PCB mixture as it enters the river (dissolved phase or particle phase dominant, resemblance to any Aroclor mixture);
- seasonal variations in the source of PCBs in the Upper Hudson;
- the factors governing PCB transport and water column concentrations such as seasonal or flow variations;

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- seasonal variations in summer water column conditions;
- suspended matter/dissolved phase distributions of PCB congeners and how closely do they approach an equilibrium distribution;
- the use of equilibrium-based assumptions to predict mean PCB transport;
- the importance of "disequilibrium" in the Upper Hudson.

While it is not anticipated that the Water Column sampling and analytical program scheduled for Phase 2A can resolve all of these issues, it is expected to clarify many of them. The results of the other Phase 2A programs, particularly the High Resolution Core Program, will also help to clarify these issues. The success of the Phase 2A effort is dependent upon both the quality of the measurements made and the actual results obtained. The individual analyses scheduled for the water column study are discussed below within the context of meeting the program data quality objectives. The analyses will be performed by contract laboratories and Lamont-Doherty Geological Observatory.

3.2.1.1 Congener Specific Water Column PCB Analyses

Three sample types will be derived from each water sample taken for the Water Column Study: a dissolved phase PCB sample, a suspended matter phase PCB sample, and a total water sample. The congener specific analysis on the dissolved and suspended matter fractions will address the following issues:

• the nature of the PCB source(s) to the river, by generating a "finger print" based on the congener mixture (e.g., a source derived from an Aroclor-like mixture vs. a highly dechlorinated sediment source);

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the effect of in situ processes such as gas exchange, aerobic degradation, and particle adsorption on the nature of the PCBs being transported at any given time or location;

 the importance of the lighter congeners in the total PCB mixture borne by the river (previous data suggest that as much as half of the total water column burden may be mono- and dichlorobiphenyls);

• the importance of other PCB sources.

The total water analyses will be performed as a supporting measurement, since the sample volume collected will be too small to permit the low level quantification of the congeners that will be achieved for the dissolved and particulate fractions.

3.2.1.2 Congener Specific Total Suspended Matter PCB Analyses

This measurement is required for the examination of suspended matter/dissolved phase partitioning of PCB congeners. Partitioning is defined on the basis of the water to solid phase-mass-ratio. Total suspended matter is also needed to calculate the total water column PCB mass load on a per-unit-volume basis. In addition, variations in the suspended matter load have important implications for variations in PCB mass load due to the high sediment partitioning normally exhibited by PCBs.

3.2.1.3 Chlorophyll-a

This parameter can be an important factor in defining the partitioning ratios of PCBs between dissolved and suspended matter phases. Several recent references suggest that suspended matter concentrations of PCBs varies directly with chlorophyll-a. The basic premise assumes that

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chlorophyll-a correlates well with in situ production of new organic material, which, in turn, provides additional sites for PCB adsorption from the water column.

3.2.1.4 Dissolved Organic Carbon (DOC)

This parameter has also been shown to affect dissolved phase/suspended matter phase partitioning of PCBs. Presumably, higher levels of dissolved organic carbon result in greater micelle formation. In turn, these micelles provide a greater capacity for the support of PCBs in a "dissolved" form.

Two methodologies will be used for this measurement. The persulfate method, to be performed by the Lamont-Doherty Geological Observatory (LDGO), represents the continuation of an existing database of DOC measurements, a data set that has been correlated with many historic water column PCB analyses. The second method represents a standard EPA water quality method which was selected since it is EPA-approved and should be comparable to the Lamont method which has not been reviewed by EPA.

3.2.1.5 pH, Temperature, and Conductivity

These parameters will be measured as standard indicators of water quality conditions.

3.2.5.6 Dissolved Oxygen

This parameter will be measured as a general indicator of water quality conditions and as a crude measure of gas exchange capabilities in various reaches of the river. It may prove most useful in examining the effect of dams and spillways in the Upper Hudson on gas exchange. These features may have important implications for loss of water-borne PCBs to the atmosphere, particularly the lightest congeners.

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3.2.2 Water Column PCB Equilibration Study

This Phase 2A experiment is designed to examine dissolved phase/suspended matter partitioning of PCB congeners. Historic data exist on the expected partition coefficients but much of it is on a homologue basis, not a congener specific basis. In addition, historic data also suggest that the in situ distributions of PCBs at some river locations are not in equilibrium. To determine the degree of non-equilibrium conditions, a set of criteria is needed to establish an effective "equilibrium" for the system. The data generated from these experiments will be used to define this effective equilibrium for the system. The experiment may also reveal what parameters affect the dissolved phase/suspended matter distribution of PCB congeners and how the congener distributions may vary with these parameters. The Equilibration Study will be performed at LDGO, with the subsequent analyses of PCB congeners in the equilibrated water performed by a contract laboratory.

3.2.2.1 Congener Specific Water Column PCB Analyses

Two sample types will be derived from water samples taken for the Equilibration Study: dissolved phase PCB and suspended matter phase PCB samples. The congener specific analysis from both phases will provide a means for estimating PCB partitioning. In conjunction with the other parameters measured as a part of the Water Column Study, the results should show the effect of various parameters on congener partitioning.

3.2.2.2 Dissolved Organic Carbon (DOC)

As mentioned previously, this parameter has been shown to affect congener partitioning in the water column. It is also a fairly reactive constituent of the water column. To ensure that measured differences between in situ congener partitioning and "equilibrated" congener partitioning are due to the dissolved phase/suspended matter exchange and not to changes in sample conditions, the DOC at the time of filtration will be measured.

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3.2.3 Confirmatory Sampling Study

The results from this study are intended for use with the geophysical investigation of the Upper Hudson described in the Phase 2A Sampling Plan. Since the planned geophysical measurements record physical river bottom properties, specifically reflectivity, there is a need to calibrate the geophysical signals obtained with a set of analytical measurements. For this reason, samples will be collected from about 100 locations in the geophysical study areas. These locations will be selected on the basis of the geophysical recordings obtained to provide a means to correlate the signals with the sediment conditions they represent, hence the title Confirmatory Sampling. On the basis of strong recommendations from the Science and Technical Committee (EPA advisory committee for this project), these samples will be stored for potential analyses subsequent to those described below. It is anticipated that any subsequent analyses would be performed only if river bottom conditions were expected to have changed between the conditions measured this fall under Phase 2A and those anticipated for Phase 2B for spring 1992. However, there may be other unanticipated reasons to perform additional analyses on these samples as well. These samples will be of particular interest if a major flood occurs between Phase 2A and Phase 2B accompanied by large-scale sediment transport. If such an event were thought to have occurred, changes in river bottom conditions could be measured by comparing the results of the Phase 2A program with those of a second geophysical survey with some additional sampling.

The sediment samples to be collected for the Confirmatory Sampling Program will be analyzed for several parameters useful for mapping sediment conditions. The analyses to be performed on the samples collected for the Confirmatory Sampling Program are listed below along with a discussion of the information they will provide.

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3.2.3.1 Grain Size Distribution

Grain size distributions will be determined by a laser particle analyzer-based methodology. This technique will be used to classify the type of sediment collected. Two sample types are planned due to the limitation of sample size. These analyses will be used to correlate the reflectivity patterns seen in the geophysical results with a quantitative description of the sediment texture. The combination of the samples along with the geophysical data should permit the classification of large areas of river bottom with respect to physical sediment properties.

The choice of a laser particle-based methodology stems from the need to classify the entire grain size distribution on the same basis. The laser particle analysis can be directly combined with standard sieve-type results since both techniques determine effective particle diameter. Thus the entire spectrum of sediment grain sizes can be examined on a consistent basis.

Small volume samples will be obtained from core slices obtained from the upper 4 to 6 inches of sediment in cores collected during this effort. In order to preserve sample stratigraphy and sufficient sample material for future analyses, small (≤ 5 gm) samples will be obtained from two-inch thick layers of the core and analyzed for grain size distribution. This analysis provides information on the fine grained portion of a sample, the fraction 1 mm in diameter or less. This is believed it be the most important sediment fraction since it will generally be high in organic carbon and readily transported under high flow conditions. It is anticipated that this sediment fraction will also contain high concentrations of PCBs relative to the remainder of the sample because of its high organic carbon content and high surface area to mass ratio.

Large volume samples will be obtained from all sampling locations. These samples will be used to determine complete grain size spectrums. For grab samples, only the large volume sample grain size analysis will be performed since presumably there will be enough material obtained to satisfy all analytical and storage needs. For locations where cores are taken, two collocated cores will

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be collected, one for slicing into thin sections and one to obtain large volume samples. In this manner, the grain size results of the thin two-inch section samples can be compared with the larger sediment sample. For these purposes, the large volume sediment sample can be thought of as a composite of the thin sections. By combining the results of the small and large volume sediment samples, it should be possible to obtain information on general sediment texture as well as on the near surface variability of the fine grained fraction. This information is needed to interpret the side-scan sonar and sub-bottom profiler data obtained as a part of the geophysical investigation.

ASTM Methods D421-85 and D422-63 including hydrometer analysis will be performed on approximately half of the large volume sediment samples procured for grain size analysis. This measurement will provide a basis for comparison between the laser-based particle analysis and a more standard technique.

3.2.3.2 X-Ray Photography of Sediment Cores

This measurement will provide information on the relative variability of sediment density down a core. This information can be correlated with sub-bottom profiler reflection horizons and actual core sections to examine sediment layering and estimate sediment layer thicknesses.

3.2.3.3 Total Carbon and Total Nitrogen

The total carbon/total nitrogen analysis is a method developed at the Lamont-Doherty Geological Observatory for the study of oceanic sediments. The method determines the total concentration of both carbon and nitrogen in the sample, including both organic and inorganic forms. The method is extremely precise and utilizes very small (<0.1 gm) samples. The analysis will also provide a measure of the sediment carbon-to-nitrogen ratio. Where inorganic carbon levels in sediments are low, the total carbon level will reflect the organic carbon content and provide a measure for either potential PCB contamination or for the potential adsorption of PCBs from other

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media. If a relationship can be established as anticipated, between total organic carbon and PCB contamination in various areas of the Hudson, then the data will be useful in interpreting PCB levels in areas where few PCB measurements exist.

The carbon-to-nitrogen (C/N) ratio can be used to indicate the presence of wood material in a sediment sample since the C/N ratio in wood is substantially larger than that for typical soil or aquatic organic material. The presence of a high C/N ratio in a sediment layer anywhere below Ft. Edward will provide a rough time horizon, since presumably this woody material was placed there subsequent to the dam removal during the floods of the mid-1970's. Historically, wood cellulose in the Upper Hudson has been associated with high levels of PCB contamination and thus an indication of its presence can provide a relative measure of potential PCB contamination in the sediments.

3.2.3.4 Total Inorganic Carbon

Total inorganic carbon will be measured by is a method developed at the Lamont- Doherty Geological Observatory for sediment analysis. Inorganic carbon content alone is a useful parameter for characterizing sediment but not essential to the investigation. However, the difference between the total carbon and the total inorganic carbon is a measure of the total organic carbon content of the sediment. This parameter, as explained above, has many important implications for sediment PCB interactions.

3.2.3.5 Total Organic Nitrogen

Total organic nitrogen will be determined using standard methodology. The difference between the total nitrogen and total organic nitrogen will give an inorganic nitrogen concentration. This way, the importance of inorganic forms of nitrogen in the sediment can be evaluated. Additionally, this measurement will help validate the use of the simple total carbon/total nitrogen ratio as a replacement for the organic carbon/organic nitrogen ratio for the examination of sediment.

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3.2.3.6 Reduction/Oxidation Potential (Redox)

Redox is a field measurement to be made on the sediment cores. Several members of the Science and Technical Committee have indicated that sediment zones of reducing potential correlate well with zones showing extensive PCB dechlorination. This measurement will serve as a rough indication of where such zones exist in the cores collected.

3.2.4 High Resolution Sediment Core Study

The Phase 2A High Resolution Sediment Core Program is intended to address several issues concerning historic PCB input, transport, and degradation. The cores collected for this program will be interpreted as records of water-borne PCB transport. Additionally, the cores provide a means to examine when and where various PCB releases to the Hudson have occurred. The specific issues to be addressed in this study include:

- recent trends in PCB levels in sediments and, by implication, recent trends in mean annual water column PCB levels;
- the nature and extent of current sources of PCBs to the Hudson;
- the nature and extent of historic input of PCBs to the Hudson;
- the rate of in situ degradation in the Upper and the Lower Hudson sediments;
- the anticipated residence time for PCBs in the sediments;
- the geochemical processes affecting sediment levels.

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The combination of analyses performed in the Water Column and Equilibration Studies along with the High Resolution Coring results will provide an extensive data base for the clarification of many of these issues. The individual measurement types scheduled for the coring study are discussed below.

3.2.4.1 Congener Specific Sediment PCB Analyses

The need for congener specific analysis for the sediments stems from the need to have an internally consistent data base among all media studied in the Phase 2A investigation.

The nature of the PCB source(s) to the river can potentially be "finger-printed" based on the congener mixture of the source (e.g., a source derived from an Aroclor-like mixture vs. a highly dechlorinated sediment source). Based on the assumption that the sediment deposited at a specific location reflects the PCB content of the suspended matter transported past that point, it is possible to resolve current sediment PCB congener mixtures which will reflect any additional PCB inputs. When a sediment core is properly dated, it is possible to establish historic conditions using the same congener specific analysis. Historic sources or transport events can be identified at various points in time by comparing sediment layers of the same age from cores distributed throughout the Hudson.

Changes in the PCB content of a sediment sample on a congener specific basis can also be used to examine the relative importance of various sources to local PCB contamination. For example, the doubling of total PCB concentrations from an upriver core to the next core downstream would suggest that between the two cores a new source of PCB contamination has been added to the river. Based on the doubling of the concentrations, the new source would appear on a local scale to be of comparable magnitude to the source present in the upriver core. The introduction of a new source would likely result in a new mixture of PCB congeners. The new congener mixture can then be used to trace the importance of the downriver source relative to the upriver source in the remaining downstream areas of the river.

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The same congener specific analysis can be used to investigate the occurrence of in situ degradation. Data in the literature, as well as research performed by several of the members of the Science and Technical Committee, indicate that the presence of certain distinct congeners and changes in the ratios of these congeners can be used to indicate degradation. To the extent that a core represents many years of deposition, "down core" variations in these properties should occur. These variations would be the result of greater degradation occurring in the older layers in the core and may permit the estimation of in situ degradation rates.

Obtaining this information may be compromised by historic variations in the PCBs deposited at a given location. Therefore, a program of analysis of archived sediment cores and sediment extracts has been proposed for Phase 2B. This program would permit the separation of the two effects (i.e. degradation vs historic PCB variations) for areas in which cores have been previously collected. It would also permit the estimation of the rate of in situ degradation since it would be possible to examine identical sediment layers 10 years or more apart. However, even if this second program is not implemented in Phase 2B, it is anticipated that the congener "finger-print" left by degradation should be readily visible in any sediments so affected relative to the anticipated Aroclor mixture sources.

The combination of congener-specific data in properly dated cores distributed throughout the Hudson will provide information on geochemical processes, PCB transport, PCB sources and the anticipated residence time of PCBs in the Hudson.

3.2.4.2 Radionuclides

Analysis of radionuclides in sediment cores provides a means of establishing the sediment core chronology. Studies of sediment cores in the Hudson have demonstrated the occurrence of well documented radionuclide events which can be used to establish sediment accumulation rates at

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various locations throughout the Hudson. By determining the activities of cesium-137, cobalt-60 and beryllium-7, it is possible to establish at least four radionuclide events in the sediments of the Lower Hudson and three in the sediments of the Upper Hudson.

<u>Cesium-137</u> is an anthropogenic radionuclide which has two distinct events associated with it. The first event corresponds to the first atmospheric atomic bomb tests in 1954, indicated in the sediments by the first appearance of cesium-137. Background levels prior to 1954 are essentially zero for this radionuclide. The second event corresponds to 1963, the year the atmospheric test ban treaty was signed. Just prior to its signing, many atmospheric tests were conducted by a number of nations. These tests are represented by a maximum in cesium-137 activity levels. A third cesium marker occurs in the Lower Hudson corresponding to the release of radioactive material to the estuary from the Indian Point nuclear power facility. This event can be separated from the 1963 maximum by the presence of cobalt-60 (see below) which was not present in the Hudson in the early 1960's.

Because of the geochemical properties of cesium-137, it can still be found in most watersheds throughout the world and, in fact, still exists at measurable levels in recent Hudson sediments. This feature of cesium chemistry generates a smooth decreasing function of cesium activity with time beginning in 1963 in the Upper Hudson.

<u>Beryllium-7</u> is a short lived, naturally occurring isotope whose presence in the sediments indicates recent deposition or interaction with surface waters within the 6 months prior to sample collection. Thus, this radionuclide can be used to initially test a core for recent deposition and provides a short term measure of the deposition rate (i.e. the thickness of the beryllium-7 containing layer divided by roughly 6 months).

<u>Cobalt-60</u> is another anthropogenic radionuclide associated with the production of atomic power. Release events for the Indian Point nuclear power facility have created additional event

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markers for the sediments of the Lower Hudson in the saline region of the estuary. The maximum release event occurred in 1971.

3.2.4.3 Total Carbon and Total Nitrogen

The total carbon/total nitrogen measurements will be the same as the technique used for the confirmatory sediment samples. Its use is also the same, as an indicator of woody material and of organic rich sediments in general. In the dated cores, the measurement of total carbon and the C/N ratio will provide insight into the interpretation of PCB deposition chronologies, sources, degradation, and transport.

3.2.4.4 Total Inorganic Carbon

Total inorganic carbon measurements will be used for the same purposes as for the Confirmatory Sampling Program, employing the same methodology.

3.2.4.5 Total Organic Nitrogen

Total organic nitrogen measurements will be used for the same purposes as for the Confirmatory Sampling Program, employing the same methodology.

3.2.4.6 Reduction/Oxidation Potential (Redox)

Redox will be measured in the cores for the same purposes as for the Confirmatory Sampling Program. It should be possible to correlate zones of reducing potential with zones showing extensive PCB dechlorination. This information will be used in the understanding of PCB degradation in the sediments.

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3.2.4.7 Grain Size Distribution

Grain size distribution will be determined for all high resolution sediment core sections. This measurement will be used in the interpretation of sediment PCB chronologies and degradation, particularly where important geochemical features correspond to changes in sediment texture. Because of the limited sample size, all core sections will analyzed using the small-volume laser-particle technique. A large volume sediment sample will be obtained from a collocated core at each location to provide information on the complete grain size spectrum at that location.

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4 **Project Organization**

The project team required to perform this remedial action plan will consist of representatives from TAMS Consultants, Inc. and Gradient Corporation, USEPA Region II, Technical Consultants, Subcontractors performing the field sampling, and Contract Analytical Laboratories. A project organizational chart is provided in Figure 4-1.

The TAMS Project Manager, Albert DiBernardo, reports directly to Douglas Tomchuk, EPA's Remedial Project Manager (RPM). TAMS will provide overall project management services for the Phase 2A sampling activities. Gradient Corporation, subcontractors to TAMS, will provide technical consulting services for chemistry and laboratory activities. Field samples will be collected by Lamont Doherty Geological Observatory (LDGO) and the Marine Science Research Center at SUNY StonyBrook (MSRC).

4.1 **Operations Responsibility**

The TAMS Project Manager will be designated to be responsible for overseeing the activities of the field team, headed by the Field Operations Leader who is responsible for ensuring that all tasks included in the Phase 2A sampling plan are completed properly. The Field Operations Leader is responsible for making field decisions regarding all field activities. Together with the Field Sampling Coordinator, they are responsible for ensuring that the field team maintains proper sampling and decontamination procedures in collecting sediment and water samples. Once samples have been collected, the Field Operations Leader will ensure that samples are properly packaged and shipped to the Analytical Laboratories.

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4.2 Laboratory Responsibilities

The TAMS/Gradient Quality Assurance Officer, Dr. A. Dallas Wait, will oversee laboratory activities of the Contract Analytical Laboratories. He will be responsible for overseeing the implementation of all technical and recording requirements of sample analyses. The selection of laboratories for this program will be based on technical capabilities and cost effectiveness with the emphasis on technical capabilities. Prior experience in EPA projects is preferable and any selected laboratory will be held in high regard by EPA. The laboratories will also be evaluated for their performance with other agencies and clients. It is important that the selected laboratories be able to obtain the lowest possible detection limits for the methods used.

The TAMS/Gradient Quality Assurance Officer will be involved with the selection of the laboratory. Selection criteria will 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

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

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Figure 4-1 Hudson River Reassessment RI/FS Phase 2A Sampling Project Organization

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5 QA Objectives for Measurement Data

The primary objective of the Quality Assurance (QA) program is to provide data of sufficient quality and quantity to assure project objectives as stated in Section 3.0 are achieved. Data quality and quantity are measured through comparison of resulting data with established acceptable limits for data precision, sensitivity, accuracy, representativeness, comparability, and completeness (PSARCC) as described in USEPA/540/G-87-003, titled "Data Quality Objectives for Remedial Response Activities." Data that have certain aspects that may be outside PSARCC QA objectives will be evaluated to determine what, if any, aspects of the data can be defensibly used to meet the RI/FS objectives. Objectives for the PSARCC parameters for this RI/FS are described in this section.

5.1 **PSARCC Objectives**

PSARCC parameter objectives have been developed for sediments, waters, and particulates based on sample objectives, analytical methods, historical data (examined in a qualitative sense) and published guidelines for EPA's Contract Laboratory Program (CLP) and New York State DEC's 1989 Analytical Services Protocol (ASP) as listed in Section 17 (References).

Data quality objectives for Phase 2A sampling are summarized on Table 5-1. Tables 5-2 and 5-3 contain PSARCC objectives for the laboratory and field analyses respectively. PSARCC parameter objectives should be achieved through the use of standardized sample collection and analysis procedures.

5.1.1 Precision

Precision measures the reproducibility of data or measurements under specific conditions. Precision is a quantitative measure of the variability of a group of data compared to their average

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value. Precision is usually stated in terms of relative percent difference or relative standard deviation. Measurement of precision is dependent upon sampling technique and analytical method. Both sampling and analysis will be as consistent as possible.

To monitor that precision, QC samples, including field and laboratory duplicate samples, and matrix spike and matrix spike duplicate recoveries will be analyzed and used to measure precision. A scheme for spiking replicate samples for PCB congeners is provided in Figure 5-1 and for conventional parameters in Figure 5-2. 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 duplicate analysis (inorganics) and matrix spike/matrix spike duplicate (organics analysis). In general, field blanks will be collected at a frequency of one per 20 water samples per day and one per 20 sediment samples. The minimum frequency of field blanks will be one per matrix per day during a continuous sampling event.

Field duplicates/replicates will be collected once for every 20 samples per matrix. Field duplicate/replicate results will be evaluated during data validation with respect to the stated DQOs.

5.1.2 Sensitivity

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

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5.1.3 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 are: laboratory error, sampling inconsistency, field contamination, laboratory contamination, handling, matrix interference, and preservation. Field and trip blanks, surrogate spikes, PE samples, as well as matrix spike QC samples will be used to measure accuracy for project samples.

5.1.4 Representativeness

Representativeness expresses the degree to which sample data represents the characteristics of the media or matrix from which it is collected. Samples that are considered representative are ones that are properly collected to accurately characterize the nature and extent of contamination at a given location. Therefore, a large number of sampling locations, a high rate of sample replication and consistent sampling methods will be implemented. Representativeness will be measured by using the methods (*e.g.* sampling, handling, and preserving) specified in the Field Sampling Plan (see Section 6). Comparison of the analytical results from field replicates will provide a direct measure of individual sample representativeness. Field replicates will be collected once for every 20 samples for the sediment, water, and particulate matrices.

5.1.5 Comparability

Comparability is a qualitative parameter expressing the confidence with which data sets can be compared. Comparability 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 and sampling methods described in this document and in the Field Sampling Plan (see Section 6). Additionally, quantitative and qualitative information on comparability will be obtained for the PCB congener

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analyses in 10% of the sediments and 5% of the waters using GC/MS confirmation by method EPA 680 modified.

5.1.6 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 extracted from applicable samples. Completeness is of the utmost concern for Phase 2A samples.

5.2 **Procedures for Monitoring PSARCC Parameters**

PSARCC parameters will be monitored through the use of procedures which have been referred to in Section 5.1. These procedures will include the use of field blanks, trip blanks, laboratory method blanks, field and laboratory duplicates or replicates, matrix spikes, duplicate matrix spikes, surrogate spikes, performance evaluations, laboratory control samples, and a careful examination of all calibration and check standards. Laboratory Control Samples (LCSs) and 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 of most use in judging analytical accuracy.

5.3 Field Measurements

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

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Documenting time and weather conditions;

Locating and determining the depth of sampling stations;

- Performing geophysical surveys;
- Determining pH, dissolved oxygen, specific conductance, and temperature of water samples.

The general QA objective for field measurement data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the intended use of the data through the documented use of standardized procedures. The procedures for performing these activities and the standardized formats for documenting them are presented in Section 6. A summary of the overall project Data Quality Objectives (DQOs) and the required levels of DQOs are presented as Table 5-4.



MS = Matrix Spike Sample MSD = Matrix Spike Duplicate Sample

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Figure 5-2 Replicate Sampling Scheme Conventional Analyses

MS = Matrix Spike Sample MD = Matrix Duplicate Sample

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Data Quality Objectives

DQO Parameter	Analyses			
Precision	Tables 5-2 and 5-3			
Accuracy	Table 5-2 and 5-3			
Sensitivity	Section 9 of the QAPP			
Representativeness	Inorganic-Aq <20% RPD @ >RDL			
	Inorganic-Sol <35% RPD @ >RDL			
	PCB congeners <10% RPD (Aq) PCB congeners <10% RPD (Sol)			
Completeness	95%			
Comparability	Based on Precision, Accuracy and Media			

Notes:

RDL	-	Required Detection Limit
RPD	=	Relative Percent Difference

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Parameter	<u>Matrix</u>	Replicate (Duplicate) Precision (% RPD)	MS/MSD ¹ Precision (% RPD)	LCS ¹ Accuracy (% Recovery)	MS/MSD Accuracy (% Recovery)	Surrogate Accuracy (% Recovery)
PCB Congeners	Water Sediment Particles	40 40 40	40 40 40	60-150 60-150 60-150	60-150 60-150 60-150	60-150 ³ 60-150 ³ 60-150 ³
Dissolved Organic Carbon	Water	20	NA	90-110	NA	NA
Dissolved Organic Carbon-Persulfate	Water	10	NA	90-110	NA	NA
Total Suspended Solids	Water	20	NA	90-110	NA	NA
Chlorophyll a	Water	20	NA	90-110	NA	NA
Weight-Loss-on- Ignition	Sediment	20	NA	90-110	NA	NA
Total Carbon/Total Nitrogen	Sediment	10 ²	NA	90-110	NA	NA
Total Inorganic Carbon	Sediment	10	NA	90-110	NA	NA
Total Organic Nitrogen	Sediment	20	NA	80-120	75-125	NA
Grain Size	Sediment	20	NA	NA	NA	NA
Radionuclides Beryllium-7 Cesium-137	Sediment	20 20	NA NA	80-120 80-120	NA NA	NA NA

Accuracy and Precision Objectives for Laboratory Analyses

¹PCB congener analyses will have 10% sediments confirmation by GC/MS method EPA 680 _____ and 5% waters confirmation by GC/MS method 680 _____ with criteria of <75% RPD between methods. ²LCS = ICV for conventional parameters ²Carbon/Nitrogen ratio must not vary by more than 10% ³Surrogates are tetrachlorometaxylene and decachlorobiphenyl.

NA = Not Applicable

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Accuracy and Precision Objectives for Field Analyses

Measurement	Instrument	Precision	Accuracy
pH	Corning Model 103	±0.1 pH units	.1 pH units
Eh	Corning Model 103	±50 millivolts	NA
Conductivity	YSI Model 33	$\pm 10/25/250 \text{ umho/cm}^1$	$\pm 5/25/250$ umho/cm ¹
Temperature	YSI Model 33	±0.1°C	±0.1°C or 1% (whichever is greater)
Dissolved Oxygen	Y51 Model 57	15%	±0.5 mg/l at full scale

¹Depends on scale being used

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Data Quality Objectives Defined as DQO Levels

Sample Matrix	Parameter	<u>Field</u>	Laboratory	DQO Level ¹
Sediment	PCB Congeners		x	v
	Loss-on-Ignition		x	v
	Total Carbon/Total Nitrogen		x	v
	Total Inorganic Carbon		x	v
	Total Organic Carbon		x	V
	Grainsize		x	v
	Radionuclides		x	v
	Eh	x		Ι
Water	PCB Congeners		x	v
	Dissolved Organic Carbon		x	v
	Dissolved Organic Carbon-Persulfate		x	v
	Total Suspended Solids		x	v
	Chlorophyll a		x	v
	Hq	x		Ι
. · · · ·	Conductivity	x		Ι
	Temperature	x		Ι
	Dissolved Oxygen	x		Ι
Particulates	PCB Congeners		x	v

¹ Defined in "Data Quality Objectives for Remedial Response Activities", USEPA/540/G-87-003 (1987).

• <u>Level V</u> - Non-standard methods. Analyses which may require method modification and/or development. <u>CLP Special Analytical Services (SAS) are considered Level V</u>.

• <u>Level I</u> - Field screening. This level is characterized by the use of portable instruments which can provide real-time data to assist in the optimization of sampling point locations and for health and safety support. Data can be generated regarding the presence or absence of certain contaminants (especially volatiles) at sampling locations.

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6 Sampling Procedures

The Phase 2A sampling program is divided into three separate sampling events:

- Confirmatory sampling for calibration of the Upper Hudson geophysical surveys,
- High resolution coring at locations throughout the Lower and Upper Hudson River, and
- Water column monitoring of the Upper Hudson River from Glens Falls to Waterford.

Confirmatory samples will be collected in order to assist in the proper interpretation of the geophysical surveys. High resolution coring will be conducted to ascertain historic trends in PCB loadings to the River at each location sampled and to evaluate PCB biodegradation in the River to the extent possible. Water column monitoring will be performed in order to determine current water-born PCB levels and congener mixtures in both dissolved and suspended matter fractions.

Sediment and water samples collected during each sampling event will be analyzed for a number of parameters. An overview of the analytical procedures to be conducted on samples collected during confirmatory sampling are found in Figures 6-1a and 6-1b. Similar overviews for the high resolution coring and water column monitoring are found in Figures 6-2 and 6-3. A summary of the number of samples to be analyzed for each parameter during each sampling event is contained in Table 6-1. Details of the selection, collection, and analysis of samples are described in the following sections of this QAPP and in the Phase 2A Sampling Plan.

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6.1 Sample Point Selection

Confirmatory samples will be collected from approximately 100 individual locations in the Upper Hudson immediately following completion of the geophysical surveys. The sampling locations will be selected based upon results of the surveys.

Sample locations for the high resolution coring have already been selected based upon information collected in the Phase I Report - Interim Characterization and Evaluation (August 1991). Cores will be collected from twelve locations in the Lower Hudson and eleven locations in the Upper Hudson. Exact locations are described and illustrated in the Phase 2A Sampling Plan-Review Copy, September 1991.

Water column monitoring stations are also defined in the Phase 2A Sampling Plan. Ten stations located between Glens Falls and Waterford have been identified. The locations are also shown in the Phase 2A Sampling Plan.

6.2 Sample Collection

6.2.1 Confirmatory Samples

Sediment samples obtained during the confirmatory sampling event will be collected by hand coring or grab sampling. Hand coring is considered the best technique since it usually involves minimal disturbance of the sediment, preserving the sediment stratigraphy. In case when hand coring is unsuccessful, grab sampling will be performed. In dense, gravel-rich sediments, it is often the only technique which will work. Based on historic data, it is anticipated that 50 core samples and 50 grab samples will be collected.

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Hand Coring

- 1. Mount a clean, decontaminated, 2.5 inch (i.d.) by 36 inch clear PVC plastic coring tube liner on the end of a hand coring apparatus. (Note that no external coring tube support is used in this technique.)
- 2. The boat or sampling platform should be positioned and stabilized over the sampling location to the extent possible. Record the exact location. (See Appendix Q for a discussion of the surveyed sample location specifications.)
- 3. Lower the apparatus with the tube attached thorough the water column vertically, tube end first until the river bottom is reached.
- 4. Gently push the apparatus into the river bottom while maintaining the apparatus vertically. The apparatus can be twisted on the vertical axis in order to obtain the maximum penetration.
- 5. Then pull the apparatus upward out of the river bottom and raise it to the surface, while maintaining the apparatus vertically.
- 6. Before or as the bottom of the tube breaks the surface, place a cap over the bottom to prevent the loss of material from the corer. Inspect the core to determine if sufficient material has been collected in an "undisturbed" manner.
- 7. If sufficient material is collected, remove the apparatus from the top of the clear coring tube and place a second cap on the top of the tube.
- 8. Rinse the tube with a small amount of river water and tape the end caps in place with Scotch Brand No. 33 electrical tape.

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- 9. Store the core vertically until it is sectioned on shore or in a laboratory.
- 10. In the event that sufficient material is not obtained, bring the tube to the surface and rinse with river water by submerging it and lifting it out of the water several times until the tube appears free of sediment. Adjust the sampling location slightly and attempt the coring again, beginning with step 3.
- 11. In the event that the hand coring technique still does not obtain acceptable results or is precluded by too great a water column depth, grab sampling may be implemented.
- 12. After the first core is collected, mount a second clean, decontaminated, 2.5 inch (i.d.) by 36 inch clear plastic coring tube liner on the end of a hand coring apparatus and obtain a second core by following steps 3 to 10. The second core should be obtained from a location more than two feet but less than five feet from the original coring location.

Grab Sampling

- 1. Attach a clean, decontaminated sampling apparatus to a rope or cable. The apparatus will consist of a metal ponar dredge or similar sediment sampler.
- 2. The boat or sampling platform should be positioned and stabilized over the sampling location to the extent possible. Record the exact location.
- 3. Set the trip mechanism and lower the apparatus to the water surface.
- 4. Then allow the sampling apparatus to free fall to the river bottom. If necessary, a weighted messenger may be sent down the cable in order to trip the grab sampler.

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- 5. Pull the apparatus back up to the boat and drain all water.
- 6. Then gently open the sampling apparatus so as to minimize disturbance of the sediments obtained.
- 7. Describe the contents of the sampling apparatus and photograph if appropriate.
- 8. Remove a portion of the least disturbed sediments and place into a clear, labeled sample container, being sure to include surface materials if they can be discerned. Place a temporary cap over the container.
- 9. In the event that the apparatus does not obtain a sufficient quantity of material for subsequent analysis, thoroughly rinse the apparatus with river water and attempt to obtain another sample. A small adjustment in the sampling location can be made if needed but the final location and all unsuccessful locations must be noted.

As indicated in Figure 6-1b, two collocated cores (two cores collected from essentially the same location) will be collected when hand coring is performed. The two collocated cores are required in order to provide enough sample for the ASTM grain size analysis. A sediment recovery of at least eight inches is required for the confirmatory sampling. Core samples will be transported to a local facility (to be determined) for X-Ray photography prior to extrusion and subsampling in the Interim Lab. The Interim Lab will consist of a mobile laboratory overseen by the Field Team Leader. The procedure to be followed once the core samples have been collected is listed below.

1. The cores are obtained from the boat or sampling platform and brought to the sample handling facility (noted in Figure 6-1 as an Interim Laboratory) while always maintaining the cores vertically.

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- Before the cores are disturbed, visually inspect the cores. Then photograph and x-ray the cores to determine density variations. Note significant features of the cores. Additional features observed during the extrusion process will also be noted.
- 3. When ready to begin separating the first core, designated in this procedure as core A, remove the top cap on the core tube gently siphon off the water overlying the sediments, taking care not to disturb the sediment water interface or to remove any sediment.
- 4. Then remove the bottom cap and replace it with a piston to be used to displace the sediments from the tube.
- 5. Push the piston upward into the tube until the sediments near the other end.
- 6. Insert a redox probe into the sediment about 1 inch (half of the planned section thickness) and wait one minute or until a stable redox potential reading is obtained.
- 7. Extrude the first 2 inches (5 cm) of sediment beyond the end of the tube and slice it off using a clean metal plate or spatula. Remove and discard the small amount of sediment on the outside perimeter of the slice. Place the remaining material in a labeled sample container. Remove portions of the sample in a representative fashion (e.g., a pie slice portion) for total carbon/total nitrogen analysis, total inorganic carbon analysis, grain size analysis by a laser technique, and total organic nitrogen. Total organic carbon will be calculated from total carbon and total inorganic carbon. Grain size analysis will only be performed on the top two or three sections extruded from the tube depending on visual features.

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If a sample layer cannot be subsectioned in a representative fashion, homogenize the sample in the sample container and then remove portions for the appropriate analyses. In the event that the sediment surface is uneven, slice the core such that the same volume of material is obtained as in a full 2 in. slice.

- Continue slicing, mixing and labelling individual sediment layers leaving the last 1 to
 2 cm of material in the core tube. The integrity of these sediments is sometimes compromised by the extrusion process and should not be used.
- 9. Then extrude the sediment from the second core, core B. Collect the first six inches (15 cm) of material. All of this material will be used for grain size determination by the ASTM method. No redox measurements will be performed on this sample. The remainder of the core will be discarded.

As indicated in Figures 6-1a and 6-1b, the total organic nitrogen analysis and grain size analyses by the laser and ASTM methods will be performed by a laboratory to be determined through the Special Analytical Services (SAS) program. All other analyses will be performed by the Lamont Doherty Geological Observatory (Lamont Doherty Laboratory).

6.2.2 High Resolution Coring

High resolution cores will be collected using either hand coring, vibra-coring, or gravity coring techniques. The hand coring technique is described in Section 6.2.1. The vibra-coring and gravity coring techniques are described below.

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Gravity Coring

- 1. Mount a clean, decontaminated, 2.5 inch (i.d.) by 36 inch clear PVC plastic coring tube liner within a gravity coring apparatus. Attach the apparatus to the end of a rope or cable to enable it to be lowered to the river bottom.
- 2. The boat or sampling platform should be positioned and stabilized over the sampling location to the extent possible. Record the exact location.
- 3. Lower the apparatus below the water surface and then allow it to free fall to the river bottom.
- 4. If needed, drive the corer further into the sediments with lead weights by dropping the weights down the cable to the corer.
- 5. Then pull the apparatus upward out of the river bottom and raise it to the surface, while maintaining the apparatus vertically.
- 6. Before or as the bottom of the tube breaks the water surface, place a cap over the bottom to prevent the loss of material from the corer. Then remove the core liner from the coring apparatus and place a cap over the top. Inspect the tube to determine if sufficient material is collected in an undisturbed manner.
- 7. Then rinse the tube with a small amount of river water and tape the end caps in place using Scotch Brand No. 33 electrical tape.
- 8. Store the core vertically until it is sectioned on shore or in a laboratory.

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9. In the event that insufficient material is collected, bring the tube to the surface and rinse it with river water by submerging it and lifting it out of the water several times until the tube appears free of sediment. Then adjust the sampling location slightly and attempt the coring again, beginning with step 3.

Vibra-coring

- 1. Mount a clean, decontaminated coring tube liner within the "vibra-coring" apparatus. Then attach the apparatus to the end of a rope or cable to enable it to be lowered to the river bottom.
- 2. The boat or sampling platform should be positioned and stabilized over the sampling location to the extent possible. Record the exact location.
- 3. Lower the apparatus to the river bottom.
- 4. Use the apparatus to obtain a core according to the manufacturer's instructions.
- 5. Pull the apparatus upward out of the river bottom and raise it to the surface, while maintaining the apparatus vertically.
- 6. If needed, before or as the bottom of the tube breaks the waster surface, place a cap over the bottom to prevent the loss of material from the corer. Then remove the core liner from the coring apparatus and place a cap over the top. Inspect the tube to determine if sufficient material was collected in an undisturbed manner.
- 7. Then rinse the tube with a small amount of river water and tape the end caps in place using Scotch Brand No. 33 electrical tape.

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8. Store the core vertically until it is sectioned on shore or in a laboratory.

As indicated in Figure 6-2, two co-located cores, designated core A and core B, will be collected at each sampling location. In addition a third core will be collected in the vicinity of the previous two cores and archived. Sediment recoveries for the high resolution coring should be at least 12 inches long. The following procedures will apply once a sediment core has been obtained:

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- 1. The cores are obtained from the boat or sampling platform and brought to the sample handling facility (typically the Lamont-Doherty Geological Observatory in the Lower Hudson and a mobile laboratory in the Upper Hudson). The cores must be maintained vertically during transport and handling at the laboratory.
- 2. At the sample handling facility, photograph the cores and note sedimentological features. Additional features are noted during the extrusion process.
- 3. When ready to begin separating the first core, core A, remove the top cap on the core tube and gently syphon off the water overlying the sediments, taking care not to disturb the sediment water interface or to remove any sediment.
- 4. Then remove the bottom cap and replace it with a piston to be used to displace the sediments from the tube.
- 5. Push the piston upward into the tube until the sediments approach the other end.
- 6. Insert a redox probe into the sediment about half of the next extrusion thickness (1 to 2 cm) and obtain a stable potential reading. A redox reading is taken for each section prior to extrusion.

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- 7. Extrude the first 2 cm of sediment beyond the end of the tube and slice it off using a clean metal plate or spatula. Remove and discard the small amount of sediment on the outside perimeter of the slice. Place the remaining sediments in a clean, labelled container for later handling. In the event that the sediment surface is uneven, slice the core such that the same volume of material as contained in a full 2 cm slice is obtained. In no case should the core be sliced less than 1 cm below the lowest point on the sediment surface.
- 8. Remove portions of the sample in a representative fashion (e.g., a pie slice portion) for PCB analysis, radionuclide analysis, grainsize, total carbon, total nitrogen, total organic nitrogen, total inorganic carbon, and loss on ignition.

If a sample cannot be subsectioned in a representative fashion, homogenize the sample in the sample container and then remove portions for the appropriate analyses.

- 9. Repeat steps 6, 7 and 8 until four sections are obtained, each time remove the peripheral material and use a clean metal plate and a clean container to collect the sediment section. In circumstances where these nominal sectioning intervals do not correspond to clear differences in the sediment layering based on grain size or other sediment physical properties, alter the core section interval to correspond to the observed boundary. Apply this approach throughout the entire core.
- 10. For the remainder of the core, extrude the sediments in 4 cm sections instead of 2 cm sections. Treat these sections in the same fashion as the 2 cm sections.

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- Continue slicing, mixing and labelling individual sediment layers leaving the last 1 to
 2 cm of material in the core tube. The integrity of these sediments is sometimes compromised by the extrusion process and should not be used.
- 12. Then extrude the sediment from the second core, core B, and subsample in a similar fashion; however, collect only the first six inches (15 cm) of material. The majority of this material will be used for grain size determination by the laser method; a small portion will be used for performing matrix spike and matrix spike duplicate (MS/MSD) analyses for PCBs. The remainder of the core will be discarded.

Figure 6-2 indicates which analyses will be conducted by a laboratory selected from SAS program and which analyses will be conducted by the Lamont Doherty Laboratory. Extrusion and subsampling of cores collected from the Lower Hudson will be conducted at the Lamont Doherty Laboratory while cores collected from the Upper Hudson may be processed at the Lamont Doherty Laboratory or a mobile laboratory.

6.2.3 Water Column Monitoring

Figure 6-3 provides an overview of analyses to be conducted on water samples collected during the water column monitoring phase of the sampling program. As indicated in Figure 6-3, three separate aliquots of water will be collected at each sampling location. A 20 liter aliquot collected in five 4 liter bottles will be filtered and analyzed for PCBs. The particulate fraction filtered from the water sample will be collected on filters and also analyzed for PCBs. A separate 1 liter aliquot of water will be collected in a 1 liter amber glass container and analyzed for PCBs without any filtering step. A third 4 liter aliquot of water will be collected and subsampled for analysis of pH and dissolved O_2 , total suspended solids, dissolved organic carbon, and Chlorophyll a. Temperature and specific conductivity will be measured in-situ prior to sampling. Dissolved O_2 and pH will be measured in the field.

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The procedure for collecting the 20 liter water sample is outlined below.

- 1. The sampling locations will be defined prior to the sampling transects via a reconnaissance visit to the prospective locations.
- Collect each sample for PCB analysis directly into clean, prepared 4 liter glass bottles.
 The cleaning procedure is described in Section 6.4
- 3. Each PCB sample will consists of 5 four liter bottles. The bottles will be filled at five points located across the river at each sampling location so as to approximately represent a cross-sectional area based mean flow condition.
- 4. At each point, lower a clean, prepared bottle to the correct sampling depth (half way between the surface and river bottom but at least 0.5 m below the surface). Trip the weighted messenger to open the bottle and once filled, quickly return the bottle to the surface. Cap and place each bottle on ice until all five bottles have been collected and the samples are ready to be filtered.
- 5. Measure conductivity and temperature at each collection point in the cross-section either during or just prior to the sample collection.
- 6. Sample the five points at each station as quickly as possible to generate a nearinstantaneous sample of the water column parameters.
- 7. For those stations where 2 twenty liter samples are required, sample each point twice in succession (i.e., two 4 liter bottles will be filled at point one, two at point 2, etc.) so as to minimize the difference between the paired samples. The second set of samples would either be considered a field duplicate and treated exactly as all other

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samples or be held for four days at the Lamont-Doherty Geological Observatory at room temperature. The bottles will be inverted once per day during this period to stir the sediment from the bottom of the bottle and speed equilibration. After four days, the sample will be filtered as described in the next section and treated in exactly the same manner as the standard water sample.

Within 4 hours of collection, each standard 20 liter sample must be separated into dissolved and suspended matter fractions (excluding those being held for a 4 day period). An empty, precleaned 4 liter amber glass bottle is necessary for performing the filtration step.

- Assemble a 6 in. stainless steel filter housing and rinse the housing with Hudson River water to equilibrate the housing with PCBs in the water. Place a clean, pre-fired, preweighed 6 in. Wattman glass fiber filter grade GF/F (0.7 μm) or equivalent, in the filter housing. The filter is pre-fired in clean, PCB free air at 450 °C overnight.
- 2. Pass the water from the first 4 liter bottle through the filter by gravity, under pressure using a pump, or by pressurizing the holding container with air. If air is used to displace the liquid then a magnetic stirring rod will be used to keep the suspended matter suspended.
- 3. Collect the filtrate in the empty 4 liter bottle. Rinse the first bottle, now empty, with a small amount of filtrate to recover any additional suspended matter still residing in the bottle. This step is repeated as necessary until no suspended material is visible on the surface of the bottle. This bottle then becomes the receiving bottle for the second 4 liter aliquot to be filtered. Continue this process until all 20 liters are filtered.

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- 4. After all 20 liters have been filtered, decant approximately 250 ml from each of the five full bottles into the empty sixth bottle. All six bottles will be sent to the SAS laboratory for analysis.
- 5. It may be necessary to use a second filter if the first filter becomes clogged. Both filters will then be treated as one suspended matter sample.
- 6. Place the filters containing the suspended matter in a labelled, clean glass jar for shipment to the Lamont Doherty Laboratory. At the Lamont Doherty Laboratory, the filters will be slowly dried (approximately 4 days) and reweighed to calculate particulate recoveries. The dried filters will be placed in glass containers and sent to the SAS laboratory for PCB congener analysis.

A procedure similar to the procedure used to collect the 20 liter water sample is used to collect the remaining aliquots of water for analysis. A 1 liter aliquot of water will be collected for analysis of PCBs. This sample will be collected in a pre-cleaned 1 liter amber glass bottle from the center point in the cross section and requires no filtration step.

An additional 4 liter aliquot of water will be collected for analysis of total suspended solids, dissolved organic carbon, Chlorophyll a, pH, and dissolved O_2 . This aliquot of water will also be collected from the center point in the cross section and treated as follows:

1. Immediately after the 4 liter aliquot of water has been collected, collect a subsample of water for total suspended solids. Decant 100 ml of water from the 4 liter bottle into a 100 ml plastic container. Seal and label the container for shipment to the SAS laboratory.

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- Place a clean, 6 in. Wattman glass fiber filter (0.7 μm) or equivalent in a 6 in. stainless steel filter housing for separation of Chlorophyll a.
- 3. Pass approximately 1 liter of water from the 4 liter bottle through the filter by gravity, under pressure using a pump, or by pressurizing the holding container with air. If air is used to displace the liquid then use a magnetic stirring rod to keep the suspended matter suspended. Collect the filtered volume in a graduated cylinder and record the volume of water filtered.
- 4. Remove the filter from the apparatus and place it in a clean, labelled, amber glass container for shipment to the SAS laboratory.
- 5. Next pass approximately 200 ml of water from the same 4 liter bottle through a nucleopore 0.45 μ m membrane filter. Collect enough filtered water to fill four 40 ml VOA vials leaving a small headspace. Use 40 VOA vials which contain 0.5 ml of 2.0 N H₂SO₄. Cap and shake vials well. After shaking, test pH of one vial to determine that a pH \leq 2 has been obtained. If not, add additional H₂SO₄ to all four vials until pH is \leq 2. Seal and label two vials for shipment to the SAS laboratory for total organic carbon analysis. Seal and label the two remaining vials for shipment to the Lamont Doherty Laboratory also for total organic carbon analysis.
- Pour a 100 200 ml aliquot of the remaining water sample into each of two 250 ml erlenmeyer flasks. Measure pH and dissolved oxygen using the procedures described in Appendices M and O.

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6.3 Sample Containers, Preservation, and Holding Times

The specific containers, preservatives, and holding times that will be utilized for this investigation are presented in Table 6-2.

6.4 Preparation of Sampling Equipment and Containers

6.4.1 Decontamination of Sampling Equipment

All decontamination and subsequent use of decontaminated equipment will be documented in a field notebook. If visual signs such as discolorations indicate that decontamination was insufficient, the equipment will be decontaminated again. If the situation persists, the equipment will be taken out of service. All properly decontaminated equipment will be wrapped in aluminum foil when not in use.

Decontamination of spatulas, mixing bowls, and other stainless steel apparatus will consist of rinsing with Hudson River water, followed by an acetone rinse and distilled deionized analyte free water rinse. After decontamination, all stainless steel apparatus and utensils will be allowed to dry and then be wrapped and stored in aluminum foil.

All filtering apparatus will be decontaminated in the laboratory prior to each days sampling events. A sufficient number of filtering apparatus will be brought in the field to complete a full day of sampling (approximately 5 - 7 units). The decontamination procedure will vary depending upon the time remaining between each days sampling activities. Prior to the initial day's sampling activities, all filtering apparatus will be decontaminated using the procedure outlined in Section 6.4.2. On subsequent days when less than 24 hours remain between sampling events, filtering apparatus will be decontaminated water rinse followed by acetone wash and a second distilled deionized water rinse. As indicated in Section 6.2.3, all filtering apparatus will be rinsed with Hudson

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River water prior to use. The intent of this last step in the decontamination procedure for filtering apparatus is not to remove all PCBs but rather to ensure that the filtering apparatus is "equilibrated" with PCB levels comparable to levels found in the water samples being filtered.

6.4.2 Preparation of Sample Containers

Glass containers supplied for PCB congener sampling and transport of total and dissolved water samples will be precleaned using the following procedure:

- 1. Wash with tap water and laboratory soap, followed by extensive tap water rinse.
- 2. Rinse with distilled water (three times).
- 3. Rinse twice with acetone (pesticide grade).
- 4. Rinse twice with hexane (pesticide grade).
- 5. Rinse twice with acetone (pesticide grade).
- 6. Stand inverted for 20 minutes to permit acetone to drain.
- 7. Heat in large, low temperature (60°C) oven at least six hours to remove last traces of organic solvents.
- 8. Cool glass container and cover with aluminum foil previously rinsed with hexane.
- 9. Secure aluminum foil cover with rubber band.

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All other glassware will be purchased "pre-cleaned" according to EPA Grade 3 level of cleanliness and used with no further clean-up.

6.5 Sample Handling and Shipment

All sediment samples collected in the field will be shipped to an Interim Laboratory (Lamont Doherty Laboratory or mobile laboratory) for extrusion and subsampling. In general, TAMS Consultants will supply all shipping coolers. Confirmatory and high resolution core samples will be shipped intact to the Interim Laboratory. Grab samples will be temporarily placed in pre-cleaned 8 oz wide mouth jars for shipment to the Interim Laboratory.

All water samples collected in the field will be placed in the appropriate containers and shipped directly to the laboratory performing the analyses (Lamont Doherty Laboratory or SAS Laboratory). The only exceptions are the large volume water samples for PCB congener analysis and some of the dissolved organic carbon samples which will be held at the Lamont Doherty Laboratory for four days and then filtered prior to being sent to the SAS Laboratory for PCB congener analysis.

Filtered particulate samples will be shipped to the Lamont Doherty Laboratory for drying and reweighing after separation in the field. After drying approximately four days, the dried filtered particulate samples will be sent to the SAS Laboratory for PCB congener analysis.

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

- The Investigation Name (Hudson River Phase 2A)
- Field Sample Number
- Sample Tag Number
- Date and Time Collected

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- Matrix
- Sampler's Name
- Preservatives Added (if applicable)
- Analysis Parameters
- Remarks

Detailed protocols for shipping samples by overnight courier are found in Appendix R.

6.6 Sample Custody

Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a completed, signed chain of custody form enclosed in each sample cooler. A copy of the chain of custody form will be retained by the Field Team Leader. Shipping containers will be secured with strapping tape and custody seals for shipment to the laboratory. Chain of custody procedures are detailed in Section 7.0 of this QAPP.

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Figure 6 - 1a Overview of Analyses Conducted for Confirmatory Sampling Grab Sampling



Figure 6-1b Overview of Analyses Conducted for Confirmatory Sampling Core Sampling



Figure 6-2 Overview of Analyses Conducted for High Resolution Coring



Figure 6 - 3 Overview of Analyses Conducted for Water Column Monitoring



Table 6-1 Approximate Number of Samples to be Collected During Phase 2A					
	Confirmatory	High	Water		
Analytical	Sediment	Resolution	Column		
Procedure	Sampling	Coring	Monitoring		
PCB (sediments)		230-276			
PCB (water, total)			77		
PCB (water, filtered)			99		
PCB (particulates)	1		99		
Dissolved Organic Carbon			99		
Dissolved Organic Carbon *			99		
Total Suspended Solids			77		
Chlorophyll A			77		
Weight Loss on Ignition (particulates)		—	99		
Weight Loss on Ignition (sediments)		230-276			
Total Inorganic Carbon	250-300	230-276			
Total Carbon/Total Nitrogen	250-300	230-276			
Total Organic Nitrogen	300	230-276			
Grain Size (ASTM)	50				
Grain Size (laser, small vol.)	125	230-276			
Grain Size (laser, large vol.)	223	23			
Radionuclides		230-276			

* Dissoled Organic Carbon by persulfate oxidation method

Table 6-2						
Sample Containers, Preservation, and Holding Times						
	I	Holding			Sample	
Parameter	Matrix	Time	Container	Preservative	Size	
PCB Congener	Sediment	5/40 days *	20 ml VOA vial	maintain at < 4 C	5-10 g	
Specific	Water (total)	5/40 days *	1 liter amber glass	maintain at < 4 C	1 liter	
GC/EDC	Water (filtered)	5/40 days *	4 liter amber glass	maintain at < 4 C	20 liter	
	Particulates	5/40 days *	amber glass	maintain at < 4 C	200 - 800 mg	
Dissolved	Water	28 days	VOA Vial	H2SO4 pH < 2	2x40 ml	
Organic Carbon				temp < 4 C		
Persulfate	Water	28 days	VOA Vial	H2SO4 pH < 2	2x40 ml	
Oxidation				temp < 4 C		
Total Suspended Solids	Water	7 days	plastic bottle	maintain at < 4 C	100 mi	
Chlorophyl A	Water	21 days	amber glass	freeze	filter	
Weight Loss on Ignition	Sediment/Particulates	none	glass	maintain at < 4 C	0.2 - 0.5 g	
Total Carbon/Total Nitrogen	Sediment	none	glass	maintain at < 4 C	5-10 mg	
Total Inorganic Carbon	Sediment	none	glass	maintain at < 4 C	50 mg	
Total Nitrogen	Sediment	none	glass	maintain at < 4 C	5-10 mg	
Total Organic Nitrogen	Sediment	28 days	glass	maintain at < 4 C	1-5 g	
ASTM Grain Size	Sediment	none	glass	none	500 g	
ASTM/Laser or equivalent	Sediment	none	glass	none	5 g or 500 g	
Radionuclides	Sediment	none	glass	maintain at < 4 C	40 - 120 g	

* Holding times are for extraction/analysis from VTSR

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7 Chain of Custody Procedures

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

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

Chain of custody establishes the documentation and control necessary to identify and trace a sample from collection to final analysis. Such documentation includes labeling to prevent mix-up, container seals to prevent unauthorized tampering with contents, secure custody, and the necessary records to support potential litigation. These precautions are crucial for a valid chain of custody. It is policy to follow the USEPA sample custody or chain of custody protocol as described in "NEIC Policies and Procedures," EPA-330/9-78-001-R, Revised May 1986. This custody is in three parts: sample collection, laboratory, 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.

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7.1 Field Specific Custody Procedures

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

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

- Where, exactly, was the sample taken?
- Who took the sample, and who witnessed it?
- Date and time of sample collection.
- Sample number, airbill number, seal number.
- Sampling conditions, i.e., type of material, weather on-site, type of sampling container and preparation, description of sampling procedure, preservation, and shipping.

The sample packaging and shipment procedures summarized below will be performed so that the samples will arrive at the laboratory with the chain of custody intact.

Field procedures will be as follows:

- The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples.
- All bottles and tubes will be tagged with sample numbers and locations.
- Sample tags will be completed for each sample using waterproof ink.

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• The Field Team Leader must review field activities to determine whether proper custody procedures were followed during the field work and decide if additional samples are required.

Transfer of custody and shipment procedures will be as follows:

- Samples will be accompanied by a properly completed chain of custody form. The sample numbers and locations will be listed on the chain-of-custody form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from sampler to another person, to a mobile laboratory, to the permanent laboratory, or to/from a secure storage area.
- Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with the completed, signed chain of custody form enclosed in each sample box or cooler. Shipping containers will be secured with strapping tape or duct tape and custody seals for shipment to the laboratory. The preferred procedure includes use of a custody seal attached to the front right and front left of the cooler. The custody seals will be covered with clear plastic tape. The cooler will be strapped shut with strapping tape in at least two locations.
- All shipments will be accompanied by the chain of custody record identifying the contents. The original record will accompany the shipment, and a copy will be retained by the Field Team Leader.
- If the samples are sent by common carrier, a bill of lading will be used. Receipts of bills of lading will be retained as part of the permanent documentation. Commercial

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carriers are not required to sign off on the custody form, as long as the custody forms are sealed inside the sample cooler, and the custody seals remain intact.

7.2 Laboratory Custody Procedures

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

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

The sample custodian will fill out a Shipment Condition Inspection Report (Figure 7-2). If problems or discrepancies are noted, they will be documented on the Inspection Report and EPA SMO will be contacted. Discrepancies in the number of samples received or sample bottle labels will also be documented on the field chain of custody form. The sample custodian will then sign and date the field chain of custody form.

After accepting custody of the samples, the sample custodian will log in the samples. Each sample will be assigned a unique sequential laboratory number which will be used for tracking the sample through the laboratory. The field chain of custody, inspection report, and airbill will then be forwarded to the laboratory project manager.

The laboratory project manager will inspect the paperwork and, if all is in order, will direct the laboratory sections to begin analysis. If problems are noted, the laboratory project manager will resolve them with the TAMS project coordinator.

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After log-in, samples will be placed in refrigerated storage pending analysis. Sample chain of custody is maintained throughout the laboratory by a system of door locks. All external doors to the laboratories will be kept locked at all times. 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.

7.3 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, pictures and subcontractor reports. All reports will be retained by EPA Region II.

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Figure 7-1 CIAIN-OF-CUSTODY RECORD

CONTRACT N	2										\wedge			l		₹	M	E			
SAMPLE AS (S)	1					1				$\overline{\}$	\sim	\mathbb{N}	\sim	\mathbb{N}	\sim	\mathbb{N}	\mathbb{N}	\mathbb{N}	\mathbb{N}		
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FIGURE 7-2 SAMPLE RECEIVING CHECKLIST SHIPMENT CONDITION INSPECTION UPON ARRIVAL

Control #: Job Code: Inspected by:	(print name)	Da Da Tin	ate Received: ate Inspected: me Inspected:					
Paperwork		Yes	No	Intact	Broken			
Airbill								
Cooler Custoo	ly Seals:							
Bottle Custod	y Seals:							
Chain of Cust	ody:	······································	·					
Traffic Repor	ts:	,	······					
Sample Tags:	- 000							
Tags Listed of								
Sample Condi	tion			.	D			
	, 	Cool	Warm	Hot	Degrees C			
Cooler Tempe	erature:		- · ·		<u></u>			
		Yes	No					
Ice:				Melted				
Bottles Broke	n:		·					
Bottles Leaking	ng:							
	-							
Preservation p	oH:	OK	Not OK	Not Check	ced			
Other		.:						
Shipment Con	dition:							
F		OK	Not OK	Major	Minor			
Problems and	Comments			•				
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Signature			Da	te				
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8 Calibration Procedures and Frequency

8.1 Field Instruments

To ensure that measurements during the investigation have been collected with properly calibrated instruments, field personnel will follow the procedures described in the instrument manufacturer's instructions and the SOPs in Appendices M through P. All field equipment will be calibrated, at a minimum, twice daily prior to and after use (with the exception of the geophysical instrumentation), maintained, and repaired in accordance with manufacturer's specifications. In addition, prior to use, each major piece of equipment will be cleaned, decontaminated, checked for damages, and repaired as needed. These activities will be noted in the field log notebook.

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

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

Instrument	<u>Appendix</u>
pH Meter	Μ
Eh Meter	N
Conductivity/Temperature Meter	0
Dissolved Oxygen Meter	Р

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8.2 Laboratory Calibration

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

Parameter	Appendix
PCB Congener	Α
Dissolved Organic Carbon	В
Dissolved Organic Carbon by Persulfate	С
Total Suspended Solids	D
Chlorophyll a	Ε
Weight-Loss-on-Ignition	F
Total Carbon/Total Nitrogen	G
Total Inorganic Carbon	H
Total Organic Nitrogen	Ι
Radionuclides	L

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Table 8-1

Equipment Maintenance and Calibration Protocols

Equipment	Maintenance/Calibration	Frequency
Conductivity meters	Internal instrumentation is factory calibrated/routinely maintained.	Every 5 years.
	A background conductivity survey will be performed to calibrate the equipment.	Prior to initiation of the geophysical survey.
pH meters	Calibrate with two pH buffer solutions.	Before use, and check prior to every sample.
Temperature	As per manufacturer's instructions	Once per day before use.
Sp. conductance	As per manufacturer's instructions	Once per day before use.
Dissolved oxygen meter	Calibration according to manufacturer's recommendations with ambient air.	At the beginning and end of each day.
Rechargeable equipment batteries	Charge.	After use as required.

Sampling accessories Periodic maintenance performed and (tubing, submersible recorded in equipment maintenance log.

As required.

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pumps)

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9 Analytical Procedures

To accomplish the objectives of the RI/FS, laboratory analyses will be performed for PCB congeners, dissolved organic carbon, dissolved organic carbon by persulfate, total suspended solids, chlorophyll a, loss-on-ignition, total carbon, total inorganic carbon, total nitrogen, total organic nitrogen, grain size distribution, and radionuclides (cesium-137, cesium-134, cobalt-60, beryllium-7, potassium-40, bismuth-214, actinium-228). 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 2A and Table 9-3 defines the detection limits required for the PCB congeners which will meet the data quality objectives of the program. Detection limit requirements for the conventional parameters are defined in Table 9-4.

Table 9-1

Analytical Procedures

Parameter	Method	Appendix
PCB Congeners	Modified NYSDEC ASP ¹	Α
Dissolved Organic Carbon	EPA Method 415.1 ²	В
Dissolved Organic Carbon for Persulfate	LDGO ³	С
Total Suspended Solids	EPA Method 160.2 ²	D
Chlorophyll a	Standard Methods - Chlorophyll a 10200H.3 ⁴	Ε
Loss-on-Ignition	LDGO ³	F
Total Carbon/Total Nitrogen	LDGO ³	G
Total Inorganic Carbon	LDGO ³	Н
Total Organic Nitrogen	Standard Methods - 4500-N(org.)C and EPA Method 351.2/351.3	I
Grainsize Distribution	ASTM ⁵ D421-85, D422-63	J
Grainsize Distribution	Laser Method	K
Radionuclides Actinium-228 Beryllium-7 Bismuth-214 Cesium-137 Cesium-134 Cobalt-60	LDGO ³	L

¹ New York State Department of Environmental Conservation, "Analytical Service Protocols", Bureau of Technical Services and Research, 1989.

² U.S. EPA, "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020 EMSL, Cincinnati, OH, Revised March 1983.

- ³ LDGO: Method utilized by Lamont Doherty Geological Observatory.
- ⁴ APHA, "Standard Methods for the Examination of Water and Wastewater", Seventeenth Edition, 1989.
- ⁵ American Society for Testing and Materials, Philadelphia, PA.

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Potassium-40

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Table 9-2

PCB Congeners

<u>BZ#</u>	PCB Congener
1	2-Chlorobiphenyl
3	4-Chlorobiphenyl
4	2.2'-Dichlorobiphenyl
5	2.3-Dichlorobiphenyl
6	2.3'-Dichlorobiphenyl
7	2,4'-Dichlorobiphenyl
9	2.5-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'-Trichlorobiphenyi
40	2,2',3,3'-Tetrachlorobiphenyl
41	2,2',3,4-Tetrachiorobiphenyi
44	2,2',3,5'-Tetrachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyi
49	2,2',4,5'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
53	2,2',5,6'-Tetrachlorobiphenyi
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-Pentachlorobiphenyi
115	2,3,4,4',6-Pentachlorobiphenyi
118	2,3',4,4',5-Pentachlorobiphenyl
119	2,3',4,4',6-Pentachlorobiphenyl
122	2',3,3',4,5-Pentachlorobiphenyl

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Table 9-2 (continued)

<u>BZ#</u>	PCB Congener
123	2',3,4,4',5-Pentachlorobiphenyi
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'-Heptachlorobiphenyi
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
185	2,2',3,4,5,5',6-Heptachlorobiphenyi
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'-OctachioroDipnenyi
200	2,2',3,3',4,5',6,6' -Octachiorooipnenyi
201	2,2',3,3',4',5,5',6-Octacniorobipnenyi
202	2,2,3,3,5,5,6,6 -Octachiorobiphenyi
200	2,2,5,5,4,4,7,5,5,7,6-Uctachioroophenyi
200	o-Nonachiorophenyl دردر عربه 4,4 دردر عربه
207	2 2' 2 2' A 5 5' 6 6' Nonachiorobiohand
200	voo - vouaciiorooipienyi کرد, ترد, عرب
209	Decacinorooipnenyi

Note:

BZ#

Ballschmitter and Zell System.

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Table 9-3

PCB Congeners - Required Detection Limits

Matrix	Homolog	Detection Limit
Particulates	Monochlorobiphenyl	2 μg/filter
	Dichlorobiphenyl through Hexachlorobiphenyl	1 μg/filter
	Heptachlorobiphenyl through Decachlorobiphenyl	1-2 µg/filter
Sediment (approx. 2 grams)	Monochlorobiphenyl	1 μg/kg
	Dichlorobiphenyl through Hexachlorobiphenyl	0.5 µg/kg
	Heptachlorobiphenyl through Decachlorobiphenyl	0.5-1 µg/kg
Water (20 liters)	Monochlorobiphenyl	0.1 μg/l
	Dichlorobiphenyl through Hexachlorobiphenyl	0.05 µg/l
	Heptachlorobiphenyl through Decachlorobiphenyl	0.05-0.1 µg/l
Water (1 liter)	Monochlorobiphenyl	1.0 μg/l
	Dichlorobiphenyl through Hexachlorobiphenyl	0.5 µg/l
	Heptachlorobiphenyl through Decachlorobiphenyl	0.5-1 µg/l

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Table 9-4

Parameter	Detection Limit
Dissolved Organic Carbon	0.5 mg/l ^a
Dissolved Organic Carbon- Persulfate	0.025 mg/l
Total Suspended Solids	0.01 mg/l ^a
Chlorophyll a	0.5 mg/m ³
Total Carbon	0.01% weight
Total Inorganic Carbon	0.02%
Total Nitrogen	0.001% weight
Total Organic Nitrogen	1.0 mg/kg ^{a,b}
Grainsize - laser method: Large volume samples Small volume samples	>4 mm to 0.001 mm distr >1 mm to 0.001 mm distr

Detection Limits for Conventional Parameters

Grainsize - ASTM Method

Radionuclides Cesium-137 Beryllium-7

Weight-Loss-on-Ignition

ibution ibution

>4 mm to 1 mm distribution

60 pcuries/kg 600 pcuries/kg

1% (on 1 gm sample)

Notes:

- Dilutions of high concentration samples may be necessary. In such cases, reported a) detection limit will be multiplied by the dilution factor and will exceed limits tabulated.
- b) Sample detection limit will be dependent upon initial weight of sample used for preparation. The detection limit may exceed the tabulated value due to preparation factors. Criteria expected is a reportable value (i.e. no "non-detects") since TON is expected to be very high in these river sediments.

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10 Data Reduction, Validation, and Reporting

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

10.1 Data Reduction

The analyst who generates the analytical data has the prime responsibility for the correctness and completeness of the data. All data will be generated and reduced following protocols specified in laboratory SOP's. 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 ensure that:

- Sample preparation information is correct and complete;
- Analysis information is correct and complete;
- The appropriate SOPs have been followed;
- Analytical results are correct and complete (including calculations);
- QC samples 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.);

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All corrections on raw data and any generated forms are made with a single-line cross-out and initialed and dated by the analyst.

The primary analyst will initial and date all documents generated by him/her. A "secondary review" of the data generated by the primary analyst will be performed. This will entail a spot-check of the above listed items. Any errors found will trigger a 100% check of all data included in that item. The secondary reviewer will initial and date all reviewed documents.

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

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

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

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10.2 Data Validation

Data validation is the process of reviewing data and accepting, qualifying, or rejecting it on the basis of sound criteria. The data generated during this program must be validated according to established guidelines in this QAPP, NYSDEC ASP (9/89) and the USEPA Region II data validation SOPs. Given the non-standard methods contained in this QAPP, the data validation approach must consist of a systematic review of the results, associated quality control methods and results, and all of the supporting data using professional judgment in areas not specifically addressed by EPA or NYSDEC Guidelines. For the PCB congener analyses, a specific data validation SOP has been developed to address the low level detection limit requirements and the congener confirmation by GC/MS. The Data Validation Guidelines for PCB congener analyses are in Appendix A-6. For all other parameters, the data validation must, at a minimum, the data validation must address the following:

Completeness:

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

- 1. Traffic Report and Chain-of-Custody (COC) forms.
- 2. Case narrative listing non-compliance issues.
- 3. Cover page and NYSDEC ASP Forms where applicable; tabulated QC results and sample results where ASP Forms are not appropriate. At a minimum these will include: tabulated sample concentrations; MS/MSD/MD results with % recoveries and % RPD per analyte; all blanks tabulated (method blanks and laboratory blanks); LCSs with % recoveries; ICVs and CCVs with

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% recoveries; holding times; % solids for sediments; surrogate recoveries; and method detection limits. Additional details are listed in Section 10.3 entitled Data Reporting.

4. Raw data supporting all analyses.

- 5. Raw data supporting all standardizations, calibrations and QC samples.
- 6. Preparation or extraction logs for all tests, matrices and samples.
- 7. % solids determination log (sediments only).
- 8. Laboratory and sampling team IDs are consistent and can be tracked throughout data.
- 9. Holding times are documented.
- Accuracy

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

% recovery - (spiked sample value - sample value) spike added x 100%

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Precision

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

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

Detection Limits

Review of data reporting limits with QAPP specific requirements.

Blank Contamination

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

The data acceptance limits for LCS, MS/MSD, MD, all blanks, ICVs and CCVs are defined within the methods and this QAPP. QC charts will be plotted for % recovery of LCS and matrix spikes samples. RPD of MD and MSD samples will be charted for this program as well. QC charts will be periodically submitted to the QA Officer for review during this program.

It is imperative that quantitation limits be kept as low as possible for all analyses. It is expected that the quantitation limits defined in Section 9 will be met. Precision and accuracy requirements have been defined in Section 5. Guidelines for acceptable surrogate standard recoveries in both waters and sediments, spike recoveries and RPD of duplicates have been defined in this

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QAPP based on NYSDEC ASP, EPA Region II criteria and technical references as listed in Section 17. These guidelines will be used in evaluating data quality.

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

- CLP Organics Data Review and Preliminary Review. March 1990, SOP No. HW-6, Rev. #7. U.S. EPA Region II.
- Evaluation of Inorganic Data for the Contract Laboratory Program. February 1990, SOP No. HW-2, Rev. X, US EPA Region II.
- 3. New York State Department of Environmental Conservation (NYSDEC) Analytical Services Protocol (ASP), September 1989, volumes 1-8.

If there are inconsistencies in criteria between the EPA and New York State DEC guidelines, the more rigorous guidelines will be adhered to.

10.3 Data Reporting

For PCB congener data, appropriate CLP forms for pesticide/PCB reporting should be used where applicable. For all parameters, data reports for each sample analyzed will include the following information at a minimum:

- Final analyte concentration.
- Laboratory sample ID#, field sample ID#, location.
- Percent solids (for sediment samples).
- Final volume of extract or prepared sample.

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- Preparation or extraction and analysis dates for holding time verifications.
- Calibration information, including (where applicable):
 - calibration curve
 - correlation coefficient, and
 - concentration response data of the calibration check standards.
- Results of the second column chromatography check including chromatograms.
- Amount of surrogate spiked and percent recovery of each surrogate.
- For matrix spike samples, the amount spiked and % recovery of each compound or analyte spiked.
- For matrix duplicate or spike duplicate samples, % RPD calculated for each compound or analyte.
- For laboratory control samples, true values and % recovery of each analyte quantitated.
- Blank results for method blanks, field blanks and laboratory analytical blanks.
- All raw data preparation and extraction logs must include:
 - analyst initials and date
 - initial and final sample volumes or weights
 - sample description artifacts (e.g. stones, standing water in sediment samples, color)
 - amount and concentration of stock spike solutions added to MS/MSD or LCS samples
 - Vendor or Lot Number identification for all initial and continuing check samples and true value concentrations of these check standards (ICV, CCV, etc.).
- All raw data analysis printouts and logs must include:
 - analyst initials and date
 - Model Number and type of instrument used for analysis

conditions of instrument (e.g. wavelength for colormetric analyses, retention times for GC, etc.)

time of start of analysis, time for all QC samples, time of end of analysis

• Method Number or SOP reference

dilutions performed and amount of sample analyzed or injected

calibration standards labeled and time recorded

QC samples and blanks clearly labeled.

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11 Internal Quality Control Checks

The type and frequency of field, matrix, and laboratory specific Quality Control (QC) checks are summarized in Tables 11.1, 11.2, and 11.3. Method SOPs must be referenced for more detailed information (in Appendices A through P of this QAPP).

11.1 Field Quality Control Checks

Quality control checks will be instituted as part of the sampling program. Field blanks will be exposed to field and sampling conditions, and analyzed by the laboratory in order to assess possible contamination from the field. A field blank will constitute deionized water passed through the field sampling apparatus (for filtered samples the field blank aliquot will be filtered), preserved as a sample, and submitted to the laboratory for analysis. The frequency of field blanks will be a minimum of 1 per decontamination event per matrix per test per day. Field replicate samples (field duplicates) will be obtained to assess the adequacy (precision) of overall sampling and handling procedures. A minimum 5% frequency for field duplicate pairs (i.e. 1 pair per 20 samples) will be taken and analyzed per matrix per analysis. For core samples, a full replicate sampling event will occur approximately 10 meters from the initial core site. One replicate set of cores will be collected from the Upper Hudson and one set from the lower Hudson. Water sample field replicates will be taken at the original occupation of the site.

11.2 Matrix Specific QC

Matrix Spike (MS)/Matrix Spike Duplicate (MSD)/Matrix Duplicate (MD) Samples: a MS/MSD pair will be performed for PCB congener analysis at the frequency of 1 per 20 samples (5%) per matrix or per SDG, whichever is more frequent. A MS/MD pair will be performed for all

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other parameters being analyzed in a laboratory (where applicable) at the 5% frequency or per SDG, whichever is more frequent. See Table 11.1 for QC summary per parameter.

The purpose of the MS is to assess matrix effects on % recovery of the compound or analyte. MS data can also be used to measure accuracy of the method with the caution that specific matrix effects may obscure the results. MSD measures the same features as MS, with the additional information on relative percent difference (RPD) between the MS and MSD. This is a measure of the precision of the method. The MD measures precision for all analytes other than the PCB congeners in this program. The % RPD between the sample and MD concentrations are determined and compared to the criteria specified in individual SOPs and in Table 11.2.

11.3 Laboratory Quality Control Checks

Table 11-4 lists criteria for laboratory QC checks. Accuracy and precision for LCS, MS/MSD/MD are given in Section 5. Reference individual SOPs in Appendices for method specific requirements. 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 1 per matrix per parameter and per each batch of 20 samples or per SDG whichever is more frequent.

Analytical Blanks

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

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

- For each parameter and each matrix, minimum of one method (procedural) blank in every batch of 20 samples or SDG whichever is more frequent will be analyzed to detect contamination.
- For each parameter and matrix (as applicable see Table 11-1) minimum of 1 laboratory control sample (LCS) per batch or every 20 samples whichever is more frequent. The LCS will be used to access laboratory performance of the method. LCS for water samples will consist of distilled deionized water spiked with the analytic of interest. LCS for PCB congener analysis of sediments will consist of Ottawa Sand (or equivalent matrix) spiked with the same standard spike mix as used for MS Samples. For most analyses in program, the ICV = the LCS for lab method evaluations. All inorganic analysis being performed for this program have the ICV defined as requiring the same preparation and analysis methods as for a sample. For this reason, the ICV can be interpreted as an LCS since it fulfills the requirements of a "blank spike sample" or "laboratory control sample". For PCB congener analysis, an LCS is required at the frequency of 1 per 20 samples extracted. For Total Organic Nitrogen, the ICV will be considered as fulfilling the QC requirements of the LCS since it will be distilled and analyzed using the same methodology as for a sample. (Additionally, "blank" sediments for spiking TON are not available therefore matrix matching the LCS is not possible.) A LCS for grainsize methods is not applicable. For the biological parameter, Chlorophyll a, the ICV will be considered equivalent to the LCS.

For PCB congeners, a minimum of 1 MS/MSD pair per matrix per batch of 20 samples or per SDG, whichever is more frequent, to assess accuracy and determine matrix effects.

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- Surrogate standards to estimate recoveries and to account for sample-to-sample variation as required in the PCB method.
- For PCB analysis, 5-point multilevel initial calibrations of instruments to establish calibration curves. For other parameters, calibrations that require linear regressions to define the curve must have r values ≥ 0.995 . These other calibrations must consist at a minimum of 4 point curve (one point = blank).
- Continuing calibration check every 5 samples for PCB congeners. For other parameters, calibration checks every 10 sample analyses (where applicable).
- Initial calibration checks or verification (ICV) performed immediately following calibration to determine accuracy of the daily calibration curve as compared to a separate source check standard. (Traceability of the ICV solution to an EPA or NBS standard solution is recommended.)
- All PCB samples will be run on a secondary column for PCB congener confirmations.
- Approximately 10% of the sediment samples and 5% of the water samples analyzed for PCBs will require additional confirmation by GC/MS using a modified version of EPA Method 680. The GC/MS analyses will be performed with the same capillary columns used for the GC/ECD analyses, and will employ similar congener standard mixes. The GC/MS analyses are intended to confirm congener identification. In addition, quantitative comparability studies between GC/EC and GC/MS will be conducted. Quantitative deviations in the results of the two methods should be less than 75 percent.

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Table 11-1Quality Control Summary

			C	luality C	ontrol P	aramete	rs		
	Method	ICV	ICB	CCV	CCB	MB	MS	MSD	MD
Laboratory Parameters									
PCB congener	Р			X	Х	Х	Х	X	
Dissolved organic carbon	E1	Х	Х	X	Х	Х			Х
Dissolved organic carbon-persulfate	L	Х	Х	X	Х	X			X
Total suspended solids	E2	X	X			Х			X
Chlorophyll a	S1	Х	X	X	X	X			Х
Weight loss-on-ignition	L	X				X			X
Total carbon/Total nitrogen	L	Х		X		Х			X
Total inorganic carbon	L	X		Х		Х			X
Total organic nitrogen	S2	X	Х	X	X	X	X		X
ASTM grainsize	A1								Х
Laser method or equivalent grainsize	A2								Х
Radionuclides	L	Х		Х		Х			Х

Methods:

- A1 = ASTM #D421-85, D422-63
- A2 = Laser method or equivalent
- P = Project specific method for PCB congeners
- S1 = Standard methods chlorophyll 10200H.3
- S2 = Standard methods TON 4500-N(org)C and EPA method 351.2

Notes:

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

- E1 = EPA method 415.1
- E2 = EPA method 160.2
- L = Lamont laboratory method

Table 11-2 **Quality Control Summary**

		Quality	Control Par	ameters	
	Matrix	Calibration	ICV	CCV	MD
Field Parameters					
pH	Water	X		X	X
Conductivity	Water	X			
Temperature	Water	X			
Dissolved Oxygen	Water	X	X		X
Redox (Eh) Potential	Sediment		X		X

Methods:

See field method SOPs in Appendix.

Notes:

pH: CCV = pH 7 buffer solution, frequency = prior to each sample analysis or every two hours, whichever is more frequent

Redox: ICV = Sensitvity check of electrode

Dissolved oxygen: ICV = distilled/deionized water

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

Table 11-3

QC Frequency Summary

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

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

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	Quality Control Parameters			
	ICB	CCV	CCB	MB
Parameter				
PCB Congener	NA	85-115	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Dissolved organic carbon	<mdl< td=""><td>90-110</td><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	90-110	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Total suspended solids	< MDL	NA	NA	<mdl< td=""></mdl<>
Chlorophyll a	< MDL	90-110	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Weight loss-on-ignition	NA	NA	NA	<mdl< td=""></mdl<>
Total carbon/Total nitrogen	NA	90-110	NA	<mdl< td=""></mdl<>
Total inorganic carbon	NA	90-110	NA	<mdl< td=""></mdl<>
Total organic nitrogen	<mdl< td=""><td>90-110</td><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	90-110	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
ASTM grain size	NA	NA	NA	NA
Laser method grain size	NA	NA	NA	NA
Radionuclides	see SOP	80-120	NA	<mdl< td=""></mdl<>
рH	NA	± 0.1 units	NA	NA
Conductivity	NA	NA	NA	NA
Temperature	NA	NA	NA	NA
Dissolved oxygen	NA	NA	NA	NA
Redox (Eh) potential	NA	NA	NA	NA

Table 11-4Criteria for Blanks and Continuing Calibrations

Notes:

PCB: Detection limit reported to be 10X blank level

NA: Not Applicable

See Section 5 for criteria on accuracy and precision using LCS (= ICV for analyses other than PCBs), MS/MSD, and MD

The quality control parameters are defined in Table 11-3

12 Performance and System Audits and Frequency

Audits of the field sampling team and of the laboratories performing work in support of this program will be performed under the direction of the Quality Assurance officer. At least one on-site audit will be performed during sampling. Pre-award audits for laboratories bidding on Special Analytical Services (SAS) requests (EPA Region II) will be performed by TAMS/Gradient for the PCB congener analysis and for the laser method grain size distribution determinations. At the discretion of the QA Officer and the Program Manager, pre-award audits may be performed for other parameters as well.

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 QAPP 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.

12.1 Field Audits

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

- Completeness and accuracy of sample Chain-of-Custody (COC) forms.
- Completeness and accuracy of sample identification labels.
- Completeness and accuracy of field notebooks.
- Following proper Health & Safety procedures as outlined in the Health & Safety Plan for this program.

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- Following specific decontamination procedures as outlined in Section 6.4 of this QAPP and delineated in the Sampling Plan for this program.
- Following specific collection, preparation, preservation and storage procedures outlined in Section 6.2 and 6.3 of this QAPP.
- Following specific calibration and analytical procedures for field parameters as outlined in field parameter SOPs in Appendices M through P of this QAPP.
- Following handling and shipping procedures outlined in Section 6.5 and Appendix R of this QAPP.

Appendix S is an example of a Field Sampling Audit Checklist.

12.2 Laboratory Audits

The 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 many of the non-routine methods of this investigation, emphasis in these audits will focus on evaluating the technical adequacy of the analyses as it pertains to program data quality objectives. In particular, the laboratory performing the PCB congener analyses will be expected to be experienced enough with the methods to employ normal scientific judgment as necessary.

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

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- Sample flow through lab and internal sample tracking
- Chain-of-Custody
- Sample storage
- Sample preparation/extraction and analysis including:
 - SOPs
 - Logbooks or benchsheets for all preparation procedures of samples, calibration standards, QC standards/check samples, blanks
 - Logbooks or benchsheets for all analytical procedures for samples, calibrations, QC checks, matrix QC samples, blanks
 - All above documentation must include:
 - analyst initials and date
 - single-line cross-out for corrections, initials and date
 - units recorded
 - method reference number or SOP reference
- QC samples documentation inclusive of items above and for all blanks, calibrations, calibration verification check samples, laboratory control samples, spikes, duplicates, spike duplicates, surrogates, control charts (were applicable)
- Data file storage including hard copy of all data, other media (disk, tape, etc)
- Laboratory safety procedures

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

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13 Preventive Maintenance Procedures and Schedules

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

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. Standard deviation of a sample is commonly used in estimating precision.

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

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.

$$RSD - 100 (s/x)$$

or

$$CV = 100 (s/x)$$

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where: RSD = relative standard deviation, or
CV = coefficient of variation
s = standard deviation
x = mean

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

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

where: D₁ = first sample value D₂ = second sample value (duplicate)

All analyses performed in this program will have a measure of precision in terms of matrix duplicates, matrix spike duplicates, field duplicates or in the case of some selected analyses, triplicates. See specific method SOPs and Section II for further details.

14.2 Accuracy

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

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

where: \overline{X} = average observed value of measurement T = "true" value

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

% Recovery - 100
$$\left| \frac{\bar{x}}{T} \right|$$

14.3 Completeness

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

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

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15 Corrective Action

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

15.1 Immediate Corrective Action

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

If a corrective action is taken as part of normal operating procedures, the collection of poor quality data will be avoided. Instrument and equipment malfunctions are amenable to this type of corrective action, and the QC procedures will include troubleshooting guides and corrective action suggestions. The actions taken will be noted in field or laboratory notebooks or benchsheets and a memorandum issued to the QA Officer within 1 day of the corrective action. No other formal documentation will be provided, unless further corrective action is necessary. These on-the-spot corrective actions are an everyday part of the QA/QC system. Corrective action during the field sampling portion of the program is most often a result of equipment failure or an operator oversight, and may require repeating a sampling event. Operator oversight is best avoided by having field crew members audit each other's work before and after a test. It is the responsibility of the Field Team Leader to ensure that all QC procedures are followed.

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

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- QC data are outside the acceptable windows for precision and accuracy;
- Blanks contain contaminants above acceptable levels (>MDLs);
- Undesirable trends are detected in spike recoveries or the relative standard deviation between duplicates;
- There are unusual changes in detection limits;
- Deficiencies are detected by the laboratory QA Director during internal audits or from the QA Officer during program audits;
- Inquiries concerning data quality are received from the client.

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

15.2 Long-Term Corrective Action

The need for long-term corrective action may be identified by standard QC procedures, control charts, performance, or system audits. Any quality problem which cannot be solved by immediate corrective action falls into the long-term category. The Laboratory QA Director shall use a system to ensure 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.

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

Documentation of the problem is important to the system. A Corrective Action Request Form (shown on Figure 15-1) or equivalent will be completed by the person finding the quality problem. This form identifies the problem, possible causes and the person responsible for action on the problem. The responsible person may be an analyst, Field Team Leader, or the QC Director. If no person is identified as responsible for action, the QC Director will investigate the situation and determine who is responsible in each case.

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

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Figure 15-1 Corrective Action Request Form

Corrective Action Request Form No.

Originator	Date
Person Responsible	Contract
for Replying	Involved
Description of problem and when is	dentified:
State cause of problem if known or	suspected:
Sequence of Corrective Action immediately. Submit all CA forms	<u>n</u>: (If no responsible person is identified, notify QA Manager to QA Manager for initial approval of CA.)
State Date, Person, and Action Plan	nned:
· · · · · · · · · · · · · · · · · · ·	
CA Initially Approved By:	Date
Final CA Approval By:	Date
Information copies to: RESPONSIBLE PERSON/DEPAR	RTMENT QC COORDINATOR:
QA MANAGER:	
DEPARTMENT MANAGER:	

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16 Quality Assurance Report To Management

Reports will be issued by the Quality Assurance Officer upon the completion of each data collection task in consultation with the Field Team Leader and the Project Manager. The reports will include an assessment of the status of the project in relation to the agreed-upon time table. The reports will also include, as appropriate, the results of the field and laboratory audits, document audits, significant quality problems discovered, and any necessary corrective action procedures. A data quality assessment and data usability report, based on all the samples and the data validation reports will be incorporated into the final report.

Reports for field and laboratory audits will be submitted within 10 days following the audit. Serious deficiencies will be reported within 1 day of the audit with corrective actions identified.

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18 List of Acronyms for QA/QC Criteria

CCB Continuing Calibration Blank

CCV Continuing Calibration Verification (Continuing Calibration Check) Sample

- COC Chain-of-Custody
- FB Field Blank
- FD Field Duplicate Sample

ICB Initial Calibration Blank

ICV Initial Calibration Verification (Initial Calibration Check) Sample

- LCS Laboratory Control Sample
- MB Method (Preparation/Extraction) Blank
- MD Matrix Duplicate Sample

MDL Method Detection Limit

MS Matrix Spike Sample

- MSD Matrix Spike Duplicate Sample
- QA Quality Assurance
- QAPP Quality Assurance Project Plan
- QC Quality Control
- **RPD** Relative Percent Difference
- **RSD** Relative Standard Deviation
- SDG Sample Delivery Group
- SOP Standard Operating Procedure

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