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Quality Assurance Project Plan for Analytical Control and Assessment Activities in the National Study of Chemical Residues in Lake Fish Tissue

Prepared for:

U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division

Prepared by:

DynCorp Environmental

Prepared under:

Sample Control Center Contract No. 68-C-98-139 and
MOBIS Contract No. GS-23F-9820, Task 68-C-00-137

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This Quality Assurance Project Plan (QAPP) presents performance and acceptance criteria and measurement quality objectives (MQOs) established for the analysis of environmental samples collected during the National Fish Tissue Study. This QAPP also describes the methods and procedures that will be followed to ensure these criteria and MQOs are met. This document addresses only the sample analysis effort; performance criteria and procedures related to sample collection are described in a separate QAPP [3].

This document was prepared in accordance with and contains each of the elements described in the most recent version of EPA QA/R-5, *EPA Requirements for Quality Assurance Project Plans for Environmental data Operations* [4]. To improve clarity, the order of certain elements in this QAPP has been modified slightly from the order presented in EPA QA/R-5. For example, in this QAPP the Project Organization section (element "A4" in QA/R-5) follows the Project Background and Project Description sections (elements "A5" and "A6" in QA/R-5).

In accordance with the instructions provided in EPA QA/R-5, this QAPP is considered to be a dynamic document that is subject to change as sample collection and analysis progresses. All changes to procedures described in this QAPP will be reviewed by the EPA Analytical Project Manager and the EPA Quality Assurance Manager to determine if the changes significantly impact the technical and quality objectives of the project. If changes are deemed to be significant, the QAPP will be revised accordingly, and revisions will be provided to all project participants listed in the QAPP distribution list.

1.0 PROJECT BACKGROUND

In 1987, the USEPA Office of Water (OW) conducted a national screening-level investigation to determine the prevalence of selected bioaccumulative pollutants in fish, and to correlate elevated fish tissue contaminant levels with pollutant sources [1]. Game fish and bottom-dwelling fish were collected from 388 locations thought to be influenced by various point and non-point sources, and fish tissue samples were analyzed to determine levels of approximately 60 contaminants, including dioxins and furans, PCBs, pesticides and herbicides, mercury, and several other organic compounds. Results of the 1987 study indicated that target analytes were present in fish tissue at many of the sampling sites, and some of the contaminants occurred at levels posing potential human health risks. OW is conducting a new four year national study of chemical residues in fish tissue, broader in scope than the 1987 study. The new study is statistically designed to provide screening level data on a larger set of fish tissue contaminants and from a greater number of water bodies than were sampled in 1987.

2.0 PROJECT DESCRIPTION

The objective of the new *National Study of Chemical Residues in Lake Fish Tissue* (herein referred to as the National Fish Tissue Study) is to estimate the national distribution of the mean levels of selected persistent, bioaccumulative, and toxic chemicals (PBT) in fish tissue from lakes and reservoirs of the continental United States. To fulfill this objective, the National Fish Tissue Study will involve the collection of predator and bottom-dwelling fish from 500 randomly-selected lakes and reservoirs of the conterminous United States (excluding the Great Lakes) over a period of 4 years (~125 lakes per year) beginning in 1999. Fish samples from a given lake and sampling period will be sent to a Sample Preparation Laboratory where they will be weighed, composited, homogenized, and sub-sampled. The sub-samples will then be sent to analytical laboratories where they will be analyzed for the PBT chemicals listed in Table 1. Details regarding the study design, including how lakes to be sampled were selected, can be found in reference [2].

Table 1. National Fish Tissue Study Target Analyses and Corresponding Analysis Methods

Analysis Method	Analyte[a]
Dioxins and Furans by Isotope Dilution High-resolution Gas Chromatography/Mass Spectrometry *(Method 1613, Revision B)*	2,3,7,8-TCDD 2,3,7,8-TCDF 1,2,3,7,8-PeCDD 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDD 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF OCDD OCDF
Total Mercury by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry ***(Method 1631, Revision B with Appendix A - Digestion procedures for total mercury in tissue, sludge and sediment)***	Mercury
Arsenic Speciation by Arsine Generation, Chromatography, and Atomic Absorption Spectrometry ***(Method 1632, Revision A)***	arsenic(III) arsenic (V) monomethylarsonic acid (MMA) dimethylarsinic acid (DMA)
Polychlorinated Biphenyls by Isotope Dilution High-resolution Gas Chromatography/Mass Spectrometry *(Method 1668, Revision A)*	167 congeners, including: 3,3',4,4'-TeCB 3,4,4',5-TeCB 2,3,3',4,4'-PeCB 2,3,4,4',5-PeCB 2,3',4,4',5-PeCB 2',3,4,4',5-PeCB 3,3',4,4',5-PeCB 2,3,3',4,4',5-HxCB 2,3,3',4,4',5'-HxCB 2,3',4,4',5,5'-HxCB 3,3',4,4',5,5'-HxCB 2,3,3',4,4',5,5'-HpCB

Analysis Method	Analyte[a]
Organo-halide Pesticides by Gas Chromatography *(Method 1656, Revision A)*	4,4 -DDD (TDE) 4,4 -DDE 4,4 -DDT Aldrin cis and trans nonachlor Dicofol Dieldrin Endosulfan sulfate Endosulfan I Endosulfan II Endrin Ethalfluralin (Sonalan) Heptachlor Heptachlor epoxide Hexachlorocyclohexane Isodrin Kepone (Chlordecone) Methoxychlor Mirex octachlorostyrene oxychlordane PCB-1016 PCB-1221 PCB-1232 PCB-1242 PCB-1248 PCB-1254 PCB-1260 Pendamethalin (Prowl) Pentachloronitrobenzene (PCNB) cis-Permethrin trans-Permethrin Toxaphene Trifluralin α -BHC α -Chlordane (cis-Chlordane) β -BHC γ -BHC (Lindane) γ -Chlordane (trans-Chlordane) δ -BHC Pentachloroanisole
Organo-phosphorus Pesticides by Gas Chromatography *(Method 1657, Revision A)*	Chloropyrifos Diazinon Disulfoton Disulfoton sulfone Disulfoton sulfoxide Ethion Paraoxon Parathion (ethyl) Terbufos Terbufos sulfoxide Terbufos sulfone

[a]Analytes other than project target analytes (e.g., additional analytes from the method lists) may also be reported. Refer to methods for list of other analytes.

Method	Analyte[a]
Semi-volatile Organic Compounds by Isotope Dilution GC/MS *(Method 1625 , Revision C?)*	1,2,4,5-Tetrachlorobenzene 1,2,4-Trichlorobenzene 1,2-Dichlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene 2,4,5-Trichlorophenol 3,3'-Dichlorobenzidine 4,4'-Methylenebis(2-chloroaniline) 4-Bromophenyl phenyl ether 4-Nonylphenol Acenaphthene Acenaphthylene Anthracene Benzo(k)fluoranthene Benzo[a]anthracene Benzo[a]pyrene Benzo[b]fluoranthene Benzo[g,h,i]perylene Benzo[j]fluoranthene Bis(2-ethylhexyl)phthalate Butyl benzyl phthalate Chrysene Dibenzo[a,h] anthrancene Di-n-butyl phthalate Diethylstilbestrol (DES) Fluoranthene Fluorene Hexachlorobenzene Hexachlorobutadiene Indeno[1,2,3-cd]pyrene Naphthalene Nitrobenzene Pentachlorobenzene Pentachlorophenol Perylene Phenanthrene Phenol Phenol, 2,4,6-tris(1,1-dimethylethyl)- Pyrene Tetrabromobisphenol A

[a]Analytes other than project target analytes (e.g., additional analytes from the method lists) may also be reported. Refer to methods for list of other analytes.

3.0 PROJECT ORGANIZATION

The Office of Science and Technology (OST) is responsible for overall management of the National Fish Tissue Study. Day-to-day responsibility for managing various aspects of the study has been delegated to the Standards and Applied Science Division (SASD) and the Engineering and Analysis Division (EAD) within OST. SASD is responsible for managing all sample collection and data analysis activities associated with this study; EAD is responsible for managing all laboratory analysis and data verification (data review) activities. Both EAD and SASD are responsible for day-to-day interaction with contractors and with other federal, state, and local authorities involved in the project.

Several federal, state, tribal, local, and contractor organizations are participating in this project. To the extent possible, partner programs, agencies, EPA regional staff, states, and tribes will be solicited to assist with sampling logistics for this study. In all cases, however, EPA will be responsible for sampling coordination and quality assurance.

EAD will contract all laboratory services needed to support this study. Due to the large and diverse number of analyses required, it is anticipated that several contract laboratories will be used. To minimize variability that could arise from sample handling and grinding, homogenizing, compositing, and aliquotting, EAD intends to contract these activities to a single "*Sample Preparation Laboratory*" that will be used throughout the duration of the study. This laboratory must be capable of performing all types of analyses required in the study (to verify the absence of contamination for each target analyte), must have sufficient capacity to receive and process all fish collected during each study year, and must be capable of preparing, compositing, and aliquotting all fish samples in an environment that is free from detectable levels of *all* target contaminants. To further minimize analytical variability, EAD hopes to select only one contract laboratory to perform each type of analysis (i.e., one laboratory will perform all dioxin/furan analyses, one laboratory will perform all organohalide pesticide analyses, etc.) for the duration of the study. It also is possible (and desirable) that one laboratory will be responsible for more than one type of analysis (e.g., one laboratory performs all of the dioxin/furan and PCB analyses) for the duration of the study. All "*Sample Analysis Laboratories*" will receive study samples from the Sample Preparation Laboratory. The Sample Preparation Laboratory will receive samples from field sampling teams or from a frozen storage repository.

Potential problems will be controlled through the use of a *Sample Control Contractor (SCC)* that will be charged with facilitating effective communication among all parties involved in the shipment and analysis of samples under this study. SCC responsibilities also will include 1) preparing and distributing field sampling kits, 2) documenting all sample shipments, problems that arise, and resolutions to those problems, 3) reviewing laboratory data to ensure that the measurement quality objectives (MQOs) detailed in Section 5 of this QAPP are met, 4) working with the laboratories and EPA to correct quality control failures, where possible, and 5) documenting the extent to which data submissions meet study MQOs. The role of the Sample Control Contractor is critical to the timely identification and resolution of shipping, laboratory, or data quality problems as soon as they occur.

Figure 1 illustrates the project organization and relationships between groups participating in the major activities to be conducted under this study. Sections 3.1 through 3.3 describe the roles and responsibilities of the individuals involved in study activities related to sample preparation and analysis. Details regarding roles of individuals involved in sample collection and handling can be found in reference [3]. Section 3.1 of this QAPP describes the responsibilities of EPA staff; Section 3.2 describes the responsibilities of the Sample Control Contractor staff, and Section 3.3 describes the responsibilities of staff at each of the contract laboratories that will support this study.

3.1 EPA Staff

3.1.1 OST Director

The OST Director, Geoffrey Grubbs, is responsible for providing financial and staff resources necessary to meet study objectives and implement study requirements described in this QAPP.

3.1.2 OST QA Manager

The OST QA Manager, William Telliard, is responsible for assisting the EPA Study Manager and Project Managers with the development and implementation of QAPPs for this study. The QA Manager also is responsible for ensuring that all QA procedures described in this QAPP are followed, reporting any deviations from this QAPP to the Project Managers, and assisting the Project Managers in implementing corrective actions necessary to resolve these deviations. The QA Manager reports directly to the OST Director.

3.1.3 OST Study Manager

The OST Study Manager, Leanne Stahl, reports directly to the OST Director and is responsible for providing overall direction concerning the study to the EPA Project Managers shown in Figure 1. The OST Study Manager also is responsible for:

- Overseeing the development and implementation of QAPP for all phases of the National Fish Tissue Study.
- Communicating study objectives to the EPA Project Managers shown in Figure 1.
- Reviewing and approving all major work products associated with the study.
- Participating in meetings with the EPA Project Managers, other EPA staff, and staff from other organizations and contractors concerning the study.
- Working with the OST QA Manager to identify corrective actions necessary to ensure that study objectives are met.
- Assisting the OST Project Manager for Sample Analysis with sample coordination activities.

3.1.4 OST Project Manager for Sample Analysis

The OST Project Manager for Sample Analysis, Cynthia Simbanin, reports directly to the OST Director, and is responsible for:

- Developing and implementing the QAPP describing the analytical activities of the National Fish Tissue Study.
- Daily oversight of EPA and contractor staff involved in activities related to analysis of samples collected in this study.
- Communicating project objectives to all EPA and contractor staff involved in the analysis of samples collected in this study.
- Reviewing and approving major deliverables related to the analysis of samples collected in this study.
- Participating in meetings with the OST Project Manager for Sample Collection, the OST QA Manager, and the OST Director concerning study objectives, schedules, and concerns.
- Providing technical assistance concerning sample analysis and data evaluation to the OST Project Manager for Sample Collection.
- Coordinating analytical method selection.
- Assisting the OST Project Manager for Sample Collection with sample coordination activities, such as sample scheduling, tracking, and kit distribution.

3.1.5 OST Project Manager for Sample Collection

The OST Project Manager for Sample Collection, Leanne Stahl, reports directly to the OST Director, and is responsible for:

- Ensuring that sample collection resources are available and ready to implement the study design.
- Technical and daily oversight of EPA and contractor staff, and staff from other institutions or agencies involved in sample collection activities related to this study.
- Communicating project objectives to all EPA and contractor staff involved in sample collection.
- Reviewing and approving major deliverables related to the collection of samples associated with this study.
- Participating in meetings with the OST Project manager for Sample Analysis, the OST QA Manager, the OST director concerning study objectives, schedules, and concerns.

3.2 Sample Control Contractor Staff

3.2.1 SCC Project Manager

The SCC Project Manager, Lynn Riddick, is responsible for acquiring and applying resources needed to ensure that project deliverables are completed on time, within budget and to client satisfaction. The Project Manager also is responsible for developing and obtaining approval of this QAPP and for ensuring that the practices required in this QAPP meet or exceed those outlined in Quality Management Plan approved for use in the SCC contract. The Project Manager reports directly to the EPA Analytical Project Manager (Cynthia Simbanin). Other responsibilities of the SCC Project Manager include:

- Working with the EPA Analytical Project Manager to address project objectives and develop a project schedule.
- Communicating project objectives to the SCC Study Coordinator (see 3.2.3).
- Monitoring performance of the SCC Study Coordinator and other SCC staff participating in this study to ensure the quality, timeliness, and responsiveness of work performed.
- Reviewing and approving major study deliverables for the analytical activities.
- Participating in meetings with EPA staff concerning study objectives, schedules, and concerns.

3.2.2 SCC QA Manager

The SCC QA Manager, Marguerite Jones, is independent of the National Fish Tissue Study. Ms. Jones is responsible for:

- Assisting the SCC Project Manager with the development and implementation of this QAPP;
- Ensuring that all QA procedures described in this QAPP are followed during the Study.
- Reporting deviations from this QAPP to the Project Manager and assisting the Project Manager in implementing corrective actions to resolve these deviations.

3.2.3 SCC Study Coordinator

The SCC Study Coordinator, Sara Conrad, reports directly to the SCC Project Manager. The SCC Study Coordinator is responsible for:

- Understanding and implementing the requirements described in this QAPP.
- Reviewing all deliverables for the analytical activities prior to submission.
- Adhering to the schedule approved for this study.

- Ensuring that all necessary corrective action procedures are documented and implemented in a timely manner.
- Communicating study objectives and requirements to the SCC Scheduling Coordinators, the SCC Data Review Team Leader, and the Database Administrator.
- Supervising daily activities of the SCC Scheduling Coordinators, Data Reviewers, and Database Administrator and assisting these individuals with the resolution of problems that arise during study implementation.
- Developing and implementing any SOPs necessary to meet the objectives of the National Fish Tissue Study.
- Day-to-day oversight of technical activities performed by SCC staff participating in the National Fish Tissue Study.
- Notifying the Project Manager of anticipated difficulties in meeting project schedules or other requirements.
- Identifying problems at the task level and resolving difficulties in consultation with the SCC Project Manager, and the EPA Analytical Project Manager.

3.2.4 SCC Scheduling Coordinators

A primary SCC Scheduling Coordinator, Christian Maynard, will be assigned to the National Fish Tissue Study. This coordinator will report directly to the SCC Study Coordinator and will be supported by a back-up Scheduling Coordinator. Responsibilities of the SCC Scheduling Coordinators include:

- Understanding and implementing all sample scheduling and tracking requirements described in this QAPP.
- Documenting and notifying the Study Coordinator of problems related to the scheduling, shipment, and tracking of samples and data.
- Working with the Study Coordinator to identify and implement corrective actions for such problems.
- Day-to-day communication and coordination with national field sampling coordinators, field sampling teams, and laboratory personnel during sample shipment and laboratory analysis.
- Preparing and submitting to the Study Coordinator reports that summarize the status of sample analysis, data reporting, and data evaluation activities.
- Entering information in and updating the automated sample and data tracking system in a timely manner.

3.2.5 SCC Data Review Manager

The SCC Data Review Manager, Lisa White, reports directly to the SCC Study Coordinator and is responsible for:

- Understanding and communicating to SCC Data Reviewers all National Fish Tissue Study requirements concerning data quality objectives, measurement quality objectives, data quality audits, data quality assessments, and data management.
- Supervising day-to-day activities of SCC Data Reviewers supporting the National Fish Tissue Study and working with the Data Reviewers and the Study Coordinator to resolve problems and implement corrective actions in a timely manner.

- Ensuring that SCC Data Reviewers adhere to all data quality audit and assessment requirements, including documentation, corrective action, and database development procedures, described in this QAPP.
- Immediately notifying the Study Coordinator of technical or resource limitations that adversely affect study schedules or requirements.
- Performing a technical review of all SCC deliverables pertaining to data quality audits and assessments before submission to the SCC Study Coordinator for final review.

3.2.6 SCC Data Reviewers

Several SCC chemists will be assigned to perform data quality audits and data quality assessments as described in this QAPP. These SCC Data Reviewers will report directly to the SCC Data Review Manager and are responsible for:

- Understanding and implementing the data quality audit and assessment requirements described in this QAPP.
- Immediately notifying the SCC Data Review Manager of technical difficulties or other problems that adversely impact study schedules.
- Working with the analytical laboratories to implement corrective actions necessary to resolve data quality problems in a timely manner and to maximize the amount of usable data generated in this study.
- Documenting all problems and corrective actions related to data quality.
- Preparing written narratives that describe the overall quality of each laboratory data submission and recommendations concerning data usability.
- Updating the automated sample and data tracking system in a timely manner.

3.2.7 SCC Database Administrator

The SCC Database Administrator, Michael Walsh will report directly to the SCC Study Coordinator and is responsible for:

- Understanding and implementing all database development and maintenance requirements described in this QAPP.
- Working with SCC Data Reviewers, the SCC Data Review Manager, and the SCC Study Coordinator to identify problems and implement corrective actions in a timely manner.
- Notifying the SCC Study Coordinator of technical or resource constraints that may adversely impact study schedules.
- Documenting database problems and corrective actions in a manner that is both timely and consistent with this QAPP.
- Preparing written database status reports as requested by the SCC Study Coordinator.

3.3 Contract Laboratories

All sample preparation and chemical analyses in this study will be performed by contract laboratories. Each laboratory contract will document detailed requirements for sample preparation, storage, homogenization, compositing, shipment, and/or analysis as well as data management, QA, confidentiality, personnel, and equipment requirements. Each contract will also stipulate that the laboratory, and any subcontract laboratory utilized by that laboratory for the purposes of supporting this study, maintain and adhere to an approved QAPP. Due to the size and complexity of this study, each contract will require that a laboratory Project Manager, a Quality Assurance Manager, and certain

laboratory staff be available and dedicated to each project. Sections 3.3.1 through 3.3.6 below describe the responsibilities of each of these staff members.

3.3.1 Laboratory Project Manager

This individual will be responsible for the overall technical laboratory activities under the EPA contract or subcontract. This individual will be responsible for planning, conducting, and supervising projects of major significance (such as the National Fish Tissue Study), and for supplying technical advice and counsel to other professionals.

3.3.2 Laboratory QA Manager

This individual will be responsible for quality assurance (QA) of all technical efforts performed under the contract, and will report directly to senior management. This individual will direct assistance, review progress, evaluate results, and make changes in methods that have been approved by SCC and EPA, design or equipment where necessary.

3.3.3 Sample Custodian

The Sample Custodian will be responsible for logging in, handling, and storing samples.

3.3.4 Laboratory Supervisors

These individuals will be responsible for all technical efforts performed within their laboratories in support of the study. They will be responsible for supervising the laboratory staff who prepare and analyze samples under their study contract.

3.3.5 GC/MS Operators, Mass Spectral Interpretation Specialists, Purge and Trap Specialists, Extraction Specialists, Inductively Coupled Plasma Spectroscopists, Atomic Absorption Spectroscopists, and Sample Prep Specialists

These individuals will be responsible for sample preparation, sample extraction, and sample analysis on a daily basis. They also will be responsible for adhering to the analytical and QA/QC requirements specified in the contract and for reporting to their supervisors any difficulties encountered.

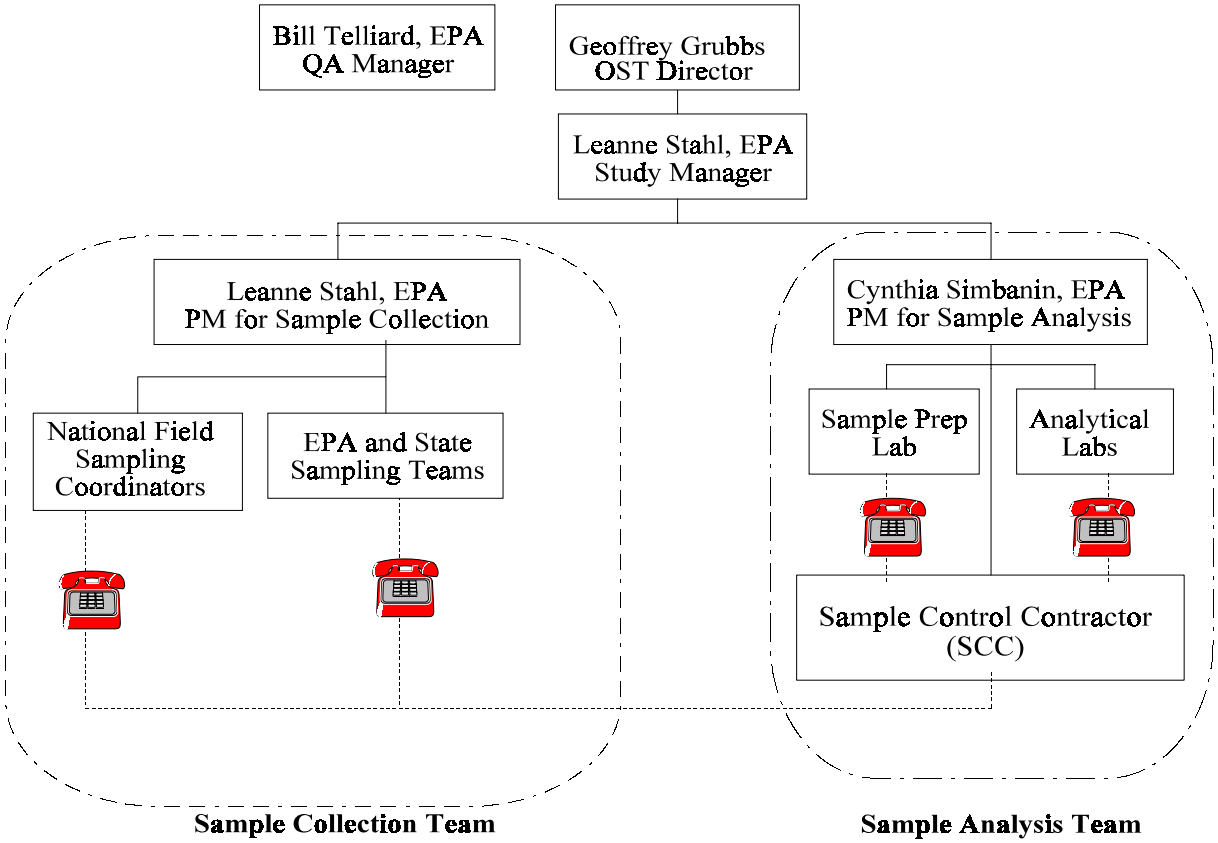
3.3.6 Systems Manager and Programmer Analysts

These individuals will be responsible for developing and maintaining any automated systems necessary to report analytical results produced under the contract and for ensuring that these systems report data in a manner that is consistent with contract requirements.

3.3.7 Data Reporting and Delivery Officer

This individual will be responsible for the organization, packaging, copying, and delivery of data deliverables submitted under the contract.

Figure 1. Project organizational chart



4.0 QUALITY OBJECTIVES

4.1 Project Quality Objectives

The National Fish Tissue Study will allow EPA OW to report on the extent of PBTs in lake fish tissue with known confidence. Therefore, study results should allow statements such as: 35% of the lakes in the U.S. have PBT levels in fish that exceed the criteria of concern, with an estimated uncertainty of ± 5%. Major sources of uncertainty include: (1) sampling from a subset of lakes rather than all lakes, (2) collecting a small number of fish (on the order of 5 to 10) from a lake relative to the total population, (3) compositing and sub-sampling the fish samples, and (4) variability in the laboratory analysis process itself. The first two sources of variability are addressed through the study design; measures for controlling these sources are described in reference [2] and [3].

The combined variability introduced by compositing fish samples, sub-sampling the composites for analysis, and laboratory analysis itself can be considered the "index" variability. Rather than prescribing a tolerable limit to "index" variability, the approach for this study is to:

(1) Prescribe sample collection procedures that would minimize "index" variability (e.g., through training of sampling crews and standardization of collection methods).

(2) Employ a sample compositing and sub-sampling scheme similar to that employed in EPA's 1997/1998 Cook Inlet Contamination Study. The sample compositing and sub-sampling procedures used in that study were shown to result in low levels of variability.

(3) Select analytical methods capable of providing the best measurement performance (e.g., low bias and acceptable and precision).

(4) Require analytical laboratories to satisfy previously established performance criteria for these analytical methods. The resulting index variability would then be estimated by collecting, compositing, and analyzing duplicate samples from 10% of the sites.

As part of its project planning activities, the OST QA Manager and OST Study Manager directed SCC to perform a review of existing methods published by EPA, other federal agencies, and in the literature. The objective of this review was to identify methods or techniques that would best meet EPA's needs for reliably measuring the targeted PBTs in tissue. OST considered techniques that best met EPA's needs to be those that a) minimized method development and validation costs, b) yielded the lowest possible detection and quantification limits, and where possible, c) avoided the use of expensive or highly novel analysis techniques that could increase analytical costs of the study.

The OST QA Manager and Study Manager invited a group of recognized experts in the field of fish tissue analysis to participate in an Analytical Methods Workgroup that would assist OST in reviewing its method selection and method development strategies. To kick off its method selection activities, OST planned to hold a meeting with workgroup members in Chicago and provided each member with a briefing book outlining the study goals, OST's method selection strategy, a list of PBTs to be targeted in the study, and several of the most promising methods identified during the literature review. The meeting was canceled due to funding constraints, but the book was distributed to planned meeting participants with a request that recipients contact OST regarding their input on the materials.

4.2 Measurement Quality Objectives

As mentioned in the previous section, "index" variability can be minimized by selecting analytical methods that provide the best available measurement performance, as gauged by standard data quality indicators (DQIs). The methods to be used in the National Fish Tissue Study reflect state-of-the-art technology and include performance criteria demonstrated to be attainable in well-operated, controlled laboratory environments. These criteria meet EPA's needs for data quality. Therefore, the general measurement quality objective for this study is to satisfy method-specific performance criteria. The following subsections and Section 11 of this QAPP provide details on how standard DQIs will be monitored and controlled in this study.

4.2.1 Precision

Precision is the degree of agreement among replicate measurements of the same property, under prescribed similar conditions [5]. It can be expressed either as a range, a standard deviation, or a percentage of the mean of the measurements (e.g., relative range or relative standard deviation).

Ideally, precision is measured by subdividing samples in the field, preserving and numbering each split separately, and sending the aliquots to the analysis laboratory as 'blind' duplicates. In this study, however, samples must be homogenized, composited, and subdivided in a strictly controlled, clean laboratory environment. Therefore, the Sample Preparation Laboratory will prepare "duplicate composite pairs" on 5% of the samples analyzed. These duplicate composite pairs will be sent to each analysis laboratory as "blind duplicates" (e.g., labeled with separate EPA sample numbers) and used to assess variability arising from the sample homogenization, compositing, aliquotting, shipping, and laboratory analysis processes. The study measurement quality objective (MQO) for analytical precision is that results from 90% of these 'duplicate composite pairs' agree within ±50% for values greater than 5x the minimum level of quantification (ML) and that 90% of these duplicate composite pairs agree within ±100% for values less than 5x the ML.

In addition to the use of these "duplicate composite pairs", all laboratories will employ EPA Office of Water's (OW's) standard suite of laboratory QC measures (e.g., initial precision and recovery samples, matrix spike and matrix spike duplicate samples) that provide information about the precision associated with various components of the analytical process. These QC elements and associated requirements are described in more detail in Section 11 (Quality Control Requirements) of this QAPP. It should be noted that performance criteria for this study are based on overall data quality, and failure to meet any single laboratory precision measure does not automatically imply the data are unacceptable for use in this study. Laboratory QC measures are used to monitor and control precision in real time so that overall precision goals are met. Details regarding the data quality assessment process governing use of data in this study are given in Sections 16, 17, and 19.

Finally, the study design specifies that 10% of the lakes will be re-sampled. The relative percent difference (RPD) between these replicated samples will provide information about the precision of data within the sub-sampled lakes. This precision measure will be affected by temporal, population, sampling, and analytical variability.

4.2.2 Bias

Bias is the systematic distortion of a measurement process that causes errors in one direction [5]. In this study, bias from the analytical process will be measured by preparing and analyzing field samples

spiked with 1) the analytes of interest (i.e., matrix spike samples), 2) isotopically labeled analogs of the target pollutants, or 3) surrogate compounds that are expected to behave in a manner similar to the target analytes. The measurement quality objective for overall analytical accuracy in this study is for 80% of the spiked field sample results to fall within the acceptance criteria specified for each method.

In addition to the use of spiked field samples, all laboratories will employ OW's standard suite of laboratory QC measures (e.g., initial precision and recovery samples, instrument calibration standards, method blanks) that provide information about the bias associated with various components of the analytical process. These QC measures and associated requirements are described in more detail in Section 11 (Quality Control Requirements) of this QAPP. It should be noted that performance criteria for this study are based on overall data quality, and failure to meet any single measure of bias does not automatically imply the data are unacceptable for use in this study. Laboratory QC measures are used to monitor and control bias in real time so that overall precision goals are met. Details regarding the data quality assessment process governing use of data in this study are given in Sections 16, 17, and 19.

4.2.3 Accuracy

Accuracy is a measure of the closeness of an individual measurement or the average of a number of measurements to the true value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that result from sampling and analytical operations. Accuracy is determined by analyzing a reference material of known pollutant concentrations or by reanalyzing a sample spiked with a known amount of pollutant. [5]

In this study, certified reference materials (CRMs), *when available,* will be sent to each laboratory annually to assess bias. CRM results will be pooled at the end of this study to determine overall study accuracy.

4.2.4 Sensitivity

Analytical sensitivity is defined as the minimum concentration of an analyte above which a data user can be reasonably confident that the analyte was reliably detected and quantified. For this study, the method detection limit (MDL) and the minimum level (ML) will be used to define the sensitivity of each measurement process.

The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. EPA procedures for determining the MDL are given at 40 CFR 136, Appendix B. [6]

The ML is defined as the lowest concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point for an analyte. It is equivalent to the concentrations of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been employed.

Ideally, analytical methods to be used in this study would have MDLs that are below all levels of concern for the target analytes. However, due to the large number of target analytes and the lack of well-established analytical methods for some of these analytes, the approach for this study is to select methods that can give the lowest MDL economically feasible. The measurement quality objective (MQO) for

detectability is that 100% of the samples be analyzed by laboratories that have demonstrated the capability to achieve the MDLs and MLs cited in Section 11.

4.2.5 Representativeness

Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population parameter at a sampling point or for an environmental condition. It is a qualitative term that is evaluated to determine whether data appropriately reflect the media and phenomenon measured or studied.[5] This study was statistically designed so that the target population of lakes is represented by a statistically valid sub-sample. Details of this design are given in reference [2].

4.2.6 Completeness

Completeness is defined in terms of the percentage of data that are collected and deemed to be acceptable for use in the study. Three measures of completeness can be defined, as follows:

Sampling Completeness: The number of valid samples collected relative to the number of samples planned for collection

Analytical Completeness: The number of valid sample measurements relative to the number of valid samples collected; and

Overall Completeness: The number of valid sample measurements relative to the number of samples planned for collection.

The analytical completeness goal in this study is that EPA obtain valid measurements from 90% of the valid samples collected. In theory, however, a lower level of completeness can still lead to a valid study. The effects of insufficient completeness will be evaluated during the data analysis phase of this study.

4.2.7 Comparability

Comparability expresses the confidence that two data sets can contribute to a common analysis and interpolation.[5] The study will require the collection and analysis of numerous samples from various parts of the country, and data will be generated from samples collected by many different sampling teams and analyzed by multiple laboratories. To ensure comparability of data generated during this study, EPA will:

- Employ standard guidelines for sample collection
- Use detailed analytical methods specifying each step of the laboratory process
- Use one laboratory per method over the four year study
- Use one method for all analyses of a given pollutant
- Use a single laboratory to weigh, homogenize, composite, sub-sample, and distribute all samples to each analysis laboratory throughout the study
- Specify method detection limits and QC acceptance criteria that must be met throughout the study
- Specify data reporting formats and units that must be used throughout the study
- Use a standardized data quality assessment process

5.0 SPECIAL TRAINING REQUIREMENTS

Field sampling teams must consist of (at a minimum) one experienced fisheries biologist, one field technician, and a quality control specialist, all of whom must have experience with the array of fisheries sampling gear types to be used. In some cases, the senior fisheries biologist may assume responsibility for site quality control. Species identification should be conducted only by experienced personnel knowledgeable of the taxonomy of species in the water bodies included in National Fish Tissue Study. Additional details on field sampling training requirements can be found in the QAPP for sample collection [3].

The laboratory contracts employed in the study will specify minimum skills required of the analysts performing work under those contracts. Required "skills" will include education and experience in using the procedures and instruments employed in this study.

Because EAD's standard data review approach will be implemented during this study (and customized to meet study needs), all SCC staff responsible for reviewing data must be experienced in performing data reviews, trained to review data in accordance with EAD's general data review guidelines, experienced in reviewing data generated with the instrumentation that will be used in this study, and familiar with the performance criteria and MQOs established for this study. For example, any SCC staff member that reviews dioxins/furans data generated during this project must have some prior experience reviewing data generated by high-resolution gas chromatography/high-resolution mass spectrometry, and must have been trained to review such data in accordance with EAD's general data review guidelines. This reviewer also must have read and understood the performance criteria and MQOs applicable to this study.

6.0 DOCUMENTATION AND RECORDS

Only documentation and records relevant to sample preparation, analysis and data review are discussed in this section. Documentation and records related to sample collection can be found in reference [3].

6.1 Sample Preparation Laboratory Records

Sample preparation laboratories will be asked to document information on sample preparation log forms to be prepared by SCC. Documentation related to sample preparation includes:

- Standard operating procedure for sample preparation, compositing, homogenization and shipment.
- Sample preparation records documenting the following information for each composite sample prepared:
  - arrival time of fish samples;
  - description of shipment upon arrival;
  - person filleting, homogenizing, and preparing composite sample;
  - information about individual fish included in samples used to prepare the composite;
  - Five-digit EPA sample number (as assigned by SCC, see Section 6.3, Data Compilation, Review, and Validation Records);
  - sub-sample aliquots generated from the composite sample;
  - sample preparation time;

- shipment date and destination of samples; and
- relevant observations made during sample preparation.

- "Traffic reports" documenting shipment of samples to analytical laboratories. (Traffic reports are standardized, EPA-generated sample tracking forms.)

6.2 Analytical Laboratory Records

All laboratories involved in this study will at a minimum be required to do the following with respect to documentation and record keeping:

- Submit summary reports of all analytical results. These summary reports must be provided in both hard copy and electronic format.
- Submit hard copies of all raw data. Raw data will include items such as quantitation reports, strip charts, spectra, bench sheets, and laboratory notebooks showing tare and sample weights, and sample volumes. Raw data also will include any other information that would allow an independent reviewer to verify the calculations performed and trace the final results to the raw data. Laboratories will be required to clearly identify each data element in their data package(s).
- Submit a written report that details any problems encountered during analysis of the samples. The written report also should include comments on the performance of any part of a method.
- Obtain pre-approval of any modifications to the analytical techniques specified and submit detailed explanations of the changes implemented.
- Report results consistently in the reporting units (e.g., µg/kg, ng/kg, etc) specified in their contract.
- Submit chain-of-custody and other sample tracking information.

6.3 Data Compilation, Review and Validation Records

SCC will create and maintain a master study file, separate files for each "episode", and data review files. For this study, an episode number will be assigned to each state for each sampling year. The field sampling teams will be using a field-assigned composite sample ID number to uniquely identify each composite. SCC will assign a unique four-digit number to each episode; this episode number will be used by EPA, the laboratories, and SCC to reference all sampling events collected by the state during that year. In addition, SCC will provide the Sample Preparation Laboratory with a series of five-digit EPA sample numbers that will be assigned to each sample after compositing and aliquotting. These five-digit EPA sample numbers will be linked to the field-assigned fish composite sample identification numbers and used by the Sample Preparation Laboratory, the analytical laboratories, SCC, and EPA to identify each sample analyzed during the study. SCC also will provide the Sample Preparation Laboratory with a list of analytical laboratories and EPA "traffic reports" for use in documenting and shipping samples to the analytical laboratories.

Cumulatively, the master file, the episode files, and the data review files will contain the following records:

- A copy of this QAPP, the sample collection activity QAPP, and the study design document;
- A copy of each laboratory statement of work;
- A summary page that documents the Episode Number, the sample numbers assigned to the Episode, the laboratories that will be analyzing each sample, the EPA contract number under which these analyses are being performed, and the date of sample collection and shipment;

- The name, address, phone number and primary contact of each laboratory preparing and analyzing samples in the episode;
- A copy of each traffic report prepared and sent with each sample;
- A list that cross-references the composite sample identification number assigned to each sample by the sample collection team against the five-digit EPA sample numbers assigned by the Sample Preparation Laboratory after homogenization, compositing, and aliquotting;
- A log of all verbal communication with laboratory staff, sample coordinators, sampling personnel, and EPA staff regarding the status or problems with the study;
- Copies of all written correspondence with laboratory staff, sampling personnel, and EPA staff regarding the study;
- All records submitted by the sample preparation and analytical laboratories;
- Complete records regarding the data review process, including a final copy of any written data review assessments and the final data submission from each laboratory; and
- A database of final analytical results associated with each field sample.

SCC will provide copies of the final laboratory summary reports, copies of any data review assessments, and a copy of the final database to EPA EAD after the data reviews are complete. SCC will retain the master file, each episode file, and complete copies of each laboratory data submission. SCC will provide copies of these materials on an as-needed basis to EPA upon request.

7.0 SAMPLING PROCESS DESIGN

Because not all lakes in the continental US can be sampled with the available resources, the approach for this study is to select a statistically representative sample from a target population of lakes. Trends in fish contamination levels for all water bodies will then be inferred from data collected from the subset of lakes and reservoirs that are visited. The target population of lakes was generated using River Reach File Version 3 (RF3). To ensure the target population included all lakes and reservoirs with an area greater than 5,000 hectares (ha), a list from multiple sources of such lakes was constructed. The list was sent to USEPA Regional Offices and subsequently to each state to verify that each lake on the list was greater than 5,000 ha and to add any lakes greater than 5,000 ha that were not on the list. The corrected list of lakes was integrated into the RF3 list of lakes before sample selection was completed.

Lakes in the target population were classified according to six size categories, with 1-5 ha and >5000 ha being the smallest and largest size categories, respectively. Of the 270,761 lakes in the target population, 172,747 belong to the 1-5 ha size category but only 241 are larger than 5000 ha. However, lakes larger than 5000 ha comprise approximately 40% of the total lake surface area, while the smaller lakes make up only 5%. If a simple random sample were selected from this target population, it is quite likely that the small lakes would dominate the sample, and that little information would be obtained from large lakes. To address this problem, lakes of different size categories were sampled with varying inclusion probabilities, with higher probabilities or weights assigned to the larger lakes so that the resulting random sample would have approximately the same number of lakes from each size category. A list of 900 randomly selected lakes was generated from the target population for sampling during the study. This represented 225 lakes per year with a total of 150 lakes in each of the six size categories of lakes included in the stratified random sampling design. The number of sites to be sampled during the study has been adjusted to the current target of 500 lakes to respond to resource constraints. This represents 125 lake per year and a total of about 80 lakes in each size category. A reserve sample set also

was generated in case an inordinate number of the lakes in the initial sample do not meet the study definition of a lake or cannot be accessed.

Further details regarding the study design and lake selection process can be found in the study design document [2] and sample collection activity QAPP [3].

8.0 SAMPLING METHOD REQUIREMENTS

Sampling method procedures and requirements are detailed in the QAPP for sample collection [3]. Some of the key requirements are summarized below.

8.1 Target Species and Sample Type

A list of preferred target predator and bottom-dwelling species has been developed for this study.[3] Following the recommendations of EPA's guidance for fish sampling in support of fish advisories [7], the primary criteria for selecting target fish for the National Fish Tissue Study are that the species: (1) are commonly consumed in the study area, (2) may potentially accumulate high concentrations of chemicals, and (3) have a wide geographic distribution. Secondarily, the target species should be: (1) easy to identify, (2) abundant, (3) easy to capture, and (4) large enough to provide adequate tissue for analysis.

The National Fish Tissue Study will focus on two distinct ecological groups of fish as target species: bottom-dwellers and predators. This permits monitoring of a wide variety of habitats, feeding strategies, and physiological factors that might result in differences in bioaccumulation of contaminants. A list of suggested target species (adapted from [7]) are listed in the study design document [2] and sample collection activity QAPP [3].

Regional, state, and tribal personnel, with their knowledge of site-specific fisheries and human consumption patterns, will aid in determinating the availability of target fish within their states. Additional target species may be added to the list of preferred targets on an as-needed basis. For example, additional Salmonid species (such as Cutthroat trout or Kokanee salmon) and Catostomid species (such as Longnose sucker, Largescale sucker, or Bridgelip sucker) may need to be added to the target species for lakes of the northwestern United States. The criteria listed above must be considered when selecting target species other than those listed in the study design document [1]. Every effort will be made to collect the desired species and number of fish; however, the outcome of field sampling efforts will ultimately depend on the natural diversity and abundance of fish in the study lakes.

Composite samples of fish fillets (for predator species) and whole fish (for bottom-dwelling species) will be collected from each sample lake. Ideally, at least five individuals per composite will be collected; a larger number can be collected if needed to provide the composite sample mass to do all the required analyses (~560 g).

Organisms used in a composite sample must:

- be of the same species;
- satisfy any legal requirements of harvestable size or weight, or at least be of consumable size if no legal harvest requirements are in effect;
- be of similar size so that the smallest individual in a composite is no less than 75 percent of the total length of the largest individual; and

- be collected at the same time (i.e., collected as close to the same time as possible but no more than 1 week apart). ***Note:*** This assumes that a sampling crew was unable to collect all fish needed to prepare the composite sample on the same day. If organisms used in the same composite are collected on different days (no more than 1 week apart), they should be frozen until all the fish to be included in the composite are delivered to the laboratory. At that time, the composite homogenate sample may be prepared.

Individual organisms used in composite samples must be of the same species because of the significant species-specific bioaccumulation potential. Accurate taxonomic identification is essential in preventing the mixing of closely related species with the target species. Under no circumstance should individuals from different species be used in a composite sample. Ideally, the target species composite should focus on the larger individuals commonly harvested by the local population.

8.2 Sample Collection Methods

Sampling teams dedicated to the National Fish Tissue Study will be equipped with an array of both active and passive gears to ensure the collection of the target numbers and species of fish. For a detailed description of sample collection methods, refer to the sample collection activity QAPP [3].

8.3 Sampling Period

The field sampling period generally will begin in August and last through November (and possibly into December in warmer regions).

9.0 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Chain of custody forms will be used for sample documentation and tracking from the field to the sample preparation laboratory. Detailed sample handling and custody requirements are given in sections 9.1 and 9.2. Briefly, they are as follows:

- Field teams will use field record forms and chain of custody forms to document information about each set of samples collected. Field teams will assign a unique 10-digit number to each composite. This number will be coded to reflect the state (2-characters), lake (4 digits), composite type (P=predator or B=bottom dweller), sample type (S=standard or D=duplicate), and year (2 digits) in which the sample was collected.
- After scaling, filleting, and compositing samples according to documentation provided by the field teams, the Sample Preparation Laboratory will create a new set of tracking paperwork for each laboratory that receives composite aliquots. This paperwork will be based on the use of 5-digit EPA sample numbers that provide no information about the sample identity. It also will include EPA Traffic Report forms, which are carbonless, multi-copy forms to facilitate sample tracking. The Sample Preparation Laboratory will forward a copy of this form to SCC for sample tracking and permanent record keeping.
- Laboratories will document the date and condition of sample at the time of receipt on their copies of the Traffic Report, and will return one copy to SCC for sample tracking and permanent record keeping.
- SCC will follow up with each scheduled recipient to verify that samples are received on time in good condition and will maintain a complete record of all sampling documentation.

Field personnel are responsible for properly identifying the samples as described below. Laboratory personnel are responsible for processing the samples as described below. All parties involved in sample handling and processing are responsible for using protocols designed to preclude contamination.

9.1 Field Requirements

A more comprehensive description of field sample handling requirements can be found in the QAPP for sample collection [3]. Key requirements are summarized below.

Species should be identified by experienced personnel as soon as fish are removed from the collection device. Non-target species or specimens of target species that do not meet size requirements will be returned to the water. Individuals of the selected target species will be rinsed in ambient water to remove any foreign material from the external surface. Each fish within the selected target species will be measured to determine total body length (mm). After initial processing, each fish found to be suitable for the composite sample will be assigned a specimen number that can range from 01 to 05. This number will identify each fish within its respective composite. A ten-character composite sample identification number consisting of the two-character state abbreviation, two-number year abbreviation, four-digit lake identification number, composite type (“P” or “B” for predator or bottom species), and sample type (“S” or “D” for standard or duplicate) will be assigned by the field teams for each composite collected. The composite sample specimen number, and information regarding the fish specimens will be recorded on the field record forms.

Each fish selected for the composite sample will be individually wrapped in cleaned (rinsed in methylene chloride and dried at 450°C for a minimum of one hour) extra heavy duty aluminum foil. Each individually wrapped fish will be placed into food-grade plastic tubing and sealed on each end with

a nylon cable tie. The fish sample identification label containing the specimen number, composite sample identification number, lake, and date of collection will be attached to the outside of each sample using one of the nylon cable ties used to seal the plastic tubing. All of the foil-wrapped and plastic tubing-sealed specimens intended for a composite sample will be kept together when possible in a large plastic bag in the same shipping container (ice chest) for transport. The sample preparation laboratories may not have personnel who can distinguish between predator and bottom-dwelling species, thus the field sampling team is responsible for indicating which samples will be filleted before homogenization. The field sampling team will accomplish this task by using a "P" or "B" as the second to the last digit in the composite number on the chain of custody form. Samples designated with a "P" are to be filleted, while those designated with a "B" are to be homogenized whole.

Once packaged, samples should be placed on dry ice for shipment. The sampling personnel must ship the samples with enough dry ice to ensure temperatures of <-20°C during shipment. Dry ice sublimes at a rate of approximately ½ lb per hour. Therefore, a minimum of 24 lbs of dry ice is recommended to ensure that the fish remain frozen for a 48 hour period, in case of shipping problems. If space, funds, and logistics permit, 36 lbs of dry ice is preferred. Samples will be shipped via Federal Express, using priority overnight service. In addition, a member of the field staff should telephone SCC to alert them to the anticipated delivery time of the samples. Field collection staff should avoid shipping samples for weekend delivery to the processing laboratory unless prior plans for such a delivery have been agreed upon with the laboratory.

Field sampling teams will ship field record forms to the sample preparation laboratory and the sample preparation laboratory will distribute the field record forms to the sampling coordinators at EPA/SASD, SCC, and Tetratech. After receiving shipping information from the field sampling team, SCC will document the information in the episode file and notify the recipient laboratory of the anticipated shipment. On the day that samples are scheduled to arrive, SCC will again contact the laboratory to confirm that samples arrived on schedule and in good condition.

9.2 Laboratory requirements

9.2.1 Sample Preparation Laboratories

Upon receipt of the fish samples, the Sample Preparation Laboratory will record the arrival time on the chain of custody form. Any observations regarding the shipment (e.g., torn or damaged packaging, insufficient dry ice) also will be documented on the chain of custody form, as well as on the sample preparation records (see Section 6.1).

The sample preparation laboratory will decontaminate any filleting instruments and surfaces as appropriate. The Sample Preparation Laboratory will weigh the fish, rinse with distilled water, scale and fillet as appropriate, homogenize, and composite fish samples following procedures that will detailed in each laboratory's contract SOW. As mentioned previously, the field sampling team should have indicated on fish sample labels and the chain-of-custody forms which fish require filleting prior to homogenization. All samples requiring compositing will be composited using the "batch" method, in which all of the individual specimens that comprise the sample are homogenized together, regardless of each individual's proportion to one another (as opposed to the "individual" method, in which equal weights of each specimen are added together).

After compositing, the Sample Preparation Laboratory will prepare one 60-gram aliquot (for semi-volatile organics), one 100-gram aliquot (for PCBs and dioxins/furans), and several 50-g aliquots (for determination of all remaining analytes and to yield extra volume for subsequent study or if samples are lost in transit). The exact number of aliquots to be prepared from each composite sample will be defined in the Sample Preparation Laboratory contract. Each aliquot will be placed in an appropriately pre-cleaned glass jar with a FEP-lined cap. The Sample Preparation Laboratory will label each sample container with the five-digit composite sample number (assigned by SCC). The Sample Preparation Laboratory also will document the sample number and the associated episode number (to be provided by SCC) on the EPA traffic report.

The Sample Preparation Laboratory will ship sample containers by Federal Express priority overnight service to the analytical laboratories in dry ice. These containers must be packaged in such a way as to prevent breakage and with enough dry ice to ensure temperatures are <-20°C during shipment. Samples also must be shipped in accordance with local, state and federal regulations. Immediately after shipping samples, the Sample Preparation Laboratory will notify SCC of the number of samples shipped, the package tracking number(s), the designated recipient(s), and the anticipated arrival date. The Sample Preparation Laboratory will retain one copy of the EPA traffic report and forward one copy to SCC. The remaining two copies will be shipped along with the samples to the analytical laboratories. After receiving shipping information from the Sample Preparation Laboratory, SCC will document the information in the episode file and notify the recipient laboratory of the anticipated shipment. On the day that samples are scheduled to arrive, SCC will again contact the laboratory to confirm that samples arrived on schedule and in good condition.

The Sample Preparation Laboratory will store any left-over composite sample in a labeled solvent-rinsed glass jar with a foil-lined plastic cap. The sample must be maintained at -20°C until archival in EPA's sample repository. Additional requirements related to sample preparation will be contained in the Sample Preparation Laboratory contract.

9.2.2 Analytical Laboratories

Upon receipt of samples from the Sample Preparation Laboratory, the analytical laboratories will sign and date the EPA traffic reports, retain one copy and return one copy to SCC to document the date and condition of samples upon receipt. Following receipt of samples at the analytical laboratories, SCC staff will maintain communication with laboratory personnel throughout the duration of analysis. The purpose of this communication is to promptly identify, resolve, and document any problems that arise during the course of analysis. In the event that samples are lost or damaged in transit, SCC will work with the laboratories, EPA, field personnel, and/or the shipping carrier to resolve the problem. SCC will document any such problems and resolutions in the episode file.

The analytical laboratories will be required to store all samples and sample aliquots at -20^{o} C prior to analysis. Additional sample handling requirements will be detailed in the laboratory contracts.

10.0 ANALYTICAL METHODS REQUIREMENTS

As indicated in Table 1, most of the target analytes can be measured using existing 1600-series EPA methods adapted to the analysis of fish tissues through the application of appropriate digestion/extraction procedures and extract clean-up techniques. Modifications of these methods to extend their applicability to fish tissue matrices will be written before the analytical phase of this study is

initiated. Where possible, analytes for which no established EPA methods exist will be measured using current literature techniques modified to include the 1600-series QA/QC elements (see Section 11.0). If necessary, more extensive method development will be pursued after a comprehensive literature search and consultation with experts in the specific area of interest. All method modifications will be tested prior to use in the study, and formal validation efforts will be employed for newly developed procedures. Method performance criteria specific to fish tissue matrices will be obtained either from existing QC data (such as for methods used in the Cook Inlet Study), or from single-laboratory validation studies to be completed before the analytical phase of this study is initiated. Where feasible, method testing and/or development of performance criteria will be performed in accordance with the procedures described for single laboratory (Tier 1) use in OW's PBMS initiative.

Sections 10.1 through 10.8 below summarize the methodologies that EPA expects to use in the National Fish Tissue Study.

10.1 Organohalide Pesticides

The target organohalide pesticides listed in Table 1 and total PCB aroclors will be analyzed by Method 1656, Revision A (*Organo-Halide Pesticides in Wastewater, Soil, Sludge, Sediment, and Tissue by GC/HSD*). These modifications were successfully employed by EPA during the 1997/1998 Cook Inlet Contaminant Study. Analysis of the target pesticides in fish tissue samples by Method 1656 involves the following steps: (1) drying a 10-g aliquot of a homogenized fish tissue sample with sodium sulfate, (2) soxhlet extraction of the dried fish sample using 1:1 methylene chloride/hexane as the extraction solvent, (3) drying with sodium sulfate and concentration of the extract to dryness (to measure lipid content) using a Kuderna-Danish and nitrogen blow-down techniques, (4) re-dissolution of the extract and lipid removal by gel-permeation chromatography and/or solid-phase extraction (SPE cartridges), (5) reconcentration of the extract using Kuderna-Danish and nitrogen blow-down techniques, and (6) quantification of the target analytes in the extract using a gas chromatograph equipped with dual capillary columns and electron capture detector. Analyte identification is performed by comparing the GC retention times of each analyte on two different columns with the respective retention times of an authentic standard. Quantitative analysis (e.g., determining the concentration of each analyte) is performed using an authentic standard to produce a calibration factor or calibration curve, and using the calibration data to determine the concentration of a pollutant in the extract. The analyte concentration in the fish tissue sample can be calculated on a mass basis (i.e., relative to the mass of the sample extracted), or lipid basis (i.e., relative to the lipid content of the sample extracted).

10.2 Organophosphorus pesticides

The target organophosphorus pesticides listed in Table 1 will be analyzed by EPA Method 1657, Revision A (*Organo-Phosphorus Pesticides in Water, Soil, and Tissue by GC/FPD*). Analysis of the target PCB congeners in fish tissue samples by Method 1657A involves the following steps: (1) drying a 10-g aliquot of a homogenized fish tissue sample with sodium sulfate, (2) soxhlet extraction of the dried fish sample using 1:1 methylene chloride/hexane as the extraction solvent, (3) drying with sodium sulfate and concentration of the extract to dryness (to measure lipid content) using a Kuderna-Danish and nitrogen blow-down techniques, (4) re-dissolution of the extract and lipid removal by gel-permeation chromatography and/or solid-phase extraction (SPE cartridges), (5) reconcentration of the extract using Kuderna-Danish and nitrogen blow-down techniques, and (6) quantification of the target analytes in the extract using a gas chromatograph equipped with dual capillary columns and flame photometric detector.

Analyte identification is performed by comparing the GC retention times of each analyte on two different columns with the respective retention times of an authentic standard. Quantitative analysis (e.g., determining the concentration of each analyte) is performed using an authentic standard to produce a calibration factor or calibration curve, and using the calibration data to determine the concentration of a pollutant in the extract. The analyte concentration in the fish tissue sample can be calculated on a mass basis (i.e., relative to the mass of the sample extracted), or lipid basis (i.e., relative to the lipid content of the sample extracted).

10.3 Dioxins/Furans

Dioxins/furans will be analyzed by EPA Method 1613, Revision B (*Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS*), EPA821-B-94-005). The method yields results for seventeen 2,3,7,8-substituted CDDs and CDFs.

Determination of dioxins/furans in tissue samples by Method 1613 involves the following steps: (1) drying a 100-g aliquot of a homogenized fish tissue sample with sodium sulfate, (2) spiking the dried fish sample with a labeled standard solution, (3) extraction either by soxhlet extraction using 1:1 methylene chloride/hexane as the extraction solvent, or acid digestion using hydrochloric acid and 1:1 methylene chloride/hexane (3) drying with sodium sulfate and concentration of the extract to dryness (to measure lipid content) using a Kuderna-Danish and nitrogen blow-down techniques, (4) re-dissolution of the extract and lipid removal by passing the extract through a layered column of silica gel, potassium silicate, and acid silica gel, (5) further clean-up of the extract using back-extraction with a strong base, acid and/or sodium chloride solution, gel-permeation chromatography, silica gel, alumina, or Florisil chromatography, (6) reconcentration of the extract using Kuderna-Danish and nitrogen blow-down techniques, and (7) quantification of the target analytes in the extract using a gas chromatograph equipped with a high-resolution mass spectrometer. Analytes are identified by comparing retention times and ion abundance ratios at two m/z's with authentic standards. Concentrations are calculated from selected ion current profile areas using either an isotope dilution or internal standard technique. The efficiency of the clean-up process is monitored by spiking the extract prior to clean-up with a labeled standard ($^{37}Cl_4$-labeled 2,3,7,8-TCDD) and tracking the final recovery of this standard. The analyte concentration in the fish tissue sample can be calculated on a mass basis (i.e., relative to the mass of the sample extracted), or lipid basis (i.e., relative to the lipid content of the sample extracted).

10.4 Polychlorinated Biphenyls

The polychlorinated biphenyl (PCB) congeners in Table 1 will be analyzed by EPA Method 1668, Revision A (*Chlorinated Biphenyls Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS* , EPA-821-R-00-002). The method yields results for 167 PCB congeners, and although twelve congeners designated as toxic by the World Health Organization (WHO) were selected as target analytes of interest in the National Fish Tissue Study, EPA will collect all of the data generated by the method.

Analysis of the target PCB congeners in fish tissue samples by Method 1668 involves the following steps: (1) drying a 10-g aliquot of a homogenized fish tissue sample with sodium sulfate, (2) spiking the dried fish sample with a labeled standard solution, (3) soxhlet extraction of the dried fish sample using 1:1 methylene chloride/hexane as the extraction solvent, (3) drying with sodium sulfate and concentration of the extract to dryness (to measure lipid content) using a Kuderna-Danish and nitrogen blow-down techniques, (4) re-dissolution of the extract and lipid removal by passing the extract through a

layered column of silica gel, potassium silicate, acid silica gel, (5) further clean-up of the extract using back-extraction with a strong base, acid and/or sodium chloride solution, gel-permeation chromatography, silica gel, carbon, or Florisil chromatography, (6) reconcentration of the extract using Kuderna-Danish and nitrogen blow-down techniques, and (7) quantification of the target analytes in the extract using a gas chromatograph equipped with a high-resolution mass spectrometer. Analytes are identified by comparing retention times and ion abundance ratios at two m/z's with authentic standards. Concentrations are calculated from selected ion current profile areas using either an isotope dilution or internal standard technique. The efficiency of the clean-up process is monitored by spiking the extract prior to clean-up with labeled standards (PCBs 81 and 111) and tracking the final recovery of these standards. The analyte concentration in the fish tissue sample can be calculated on a mass basis (i.e., relative to the mass of the sample extracted), or lipid basis (i.e., relative to the lipid content of the sample extracted).

10.5 Semi-Volatile Organics

The remainder of the target organic pollutants will be analyzed by EPA Method 1625, Revision C (*Semi-volatile Organic Compounds by Isotope Dilution GCMS*). Analysis of the target pollutants by Method 1625 will involve 1) homogenizing and spiking isotopically labeled analogs of each target compound into the sample, 2) extracting the sample at pH 12-13 and then at pH <2 with methylene chloride using continuous extraction techniques, 3) drying each extract over sodium sulfate, 4) concentrating the extract to five mL, 5) cleaning the extract with gel permeation chromatography, 6) concentrating the extract to 0.5 mL, 7) adding internal standards to the extract, and 8) injecting a one μL aliquot of the extract into a gas chromatograph (GC). The compounds are then separated by GC and detected by a mass spectrometer (MS). The labeled compounds serve to correct the variability of the analytical technique. Compound identification is performed by comparing mass spectrum and retention time to calibration standards (for most analytes) or through reference libraries through forward search or reverse search techniques. Quantitative analysis is performed in one of three ways using extracted ion current profile (EICP) areas: 1) for compounds in which standards and labeled analogs are available, the concentration is determined using isotope dilution techniques, 2) for compounds in which standards are available but labeled analogs are not, the concentration is determined using an internal standard technique, and 3) for compounds in which neither standards nor known response factors are available, concentrations are determined using the sum of the EICP areas relative to the sum of the EICP areas of the internal standard.

10.6 Total Mercury

Total mercury (Hg) will be analyzed by EPA Method 1631, Revision B (*Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*) and its Appendix *(Digestion Procedures for the Determination of Total Mercury in Tissues, Sludge, Sediments, and Soils)*. Procedures given in the appendix were successfully employed during EPA's 1997/1998 Cook Inlet Contaminant Study. They also were validated in a separate 1999 study conducted by EPA EAD. Analysis of total Hg in fish tissue samples by Method 1631 will involve the following steps: (1) a 0.5 to 1.5 gram of tissue sample is digested and refluxed with 10 mLs concentrated nitric acid, (2) the digestate is diluted to volume (50 or 100 mL) with 0.02N BrCl to ensure complete oxidation of methyl mercury, (3) aliquots of the diluted digestate are pipetted into pre-purged SnCl2-containing water, (4) Hg(0) is purged from solution onto a gold trap, and (5) Hg(0) is thermally desorbed from the gold trap and transferred to a

cold vapor atomic fluorescence spectrometer for quantification. The analyte concentration in the fish tissue sample is calculated on a mass basis (i.e., relative to the mass of the sample extracted).

10.7 Arsenic Speciation

The National Fish Tissue Study will include the determination of arsenic (III), arsenic (V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and inorganic arsenic in fish tissue samples. These species, along with total inorganic arsenic, will be determined by Method 1632, Revision A (*Chemical Speciation of Arsenic in Water and Tissue using Hydride Generation Quartz Furnace Atomic Adsorption Spectrometry*). (Although it is commonly found in fish, arsenobetaine will not be targeted in the study because of its low toxicity to fish and humans.) Method 1632A reflects procedures developed by Battelle Laboratories and used in EPA's Cook Inlet Study (8). In this technique, arsenic (III), arsenic (V), MMA, and DMA are volatilized from solution at a specific pH after reduction to the corresponding arsines with sodium borohydride. The volatilized arsines are then swept onto a liquid nitrogen cooled chromatographic trap which, upon warming, allows for a separation of species based on boiling points. The released arsines are swept by helium carrier gas into a quartz cuvette burner cell, where they are decomposed to atomic arsenic. Arsenic concentrations are determined by atomic absorption spectroscopy. Strictly speaking, this technique determines the valence states of arsenate (V) and arsenite (III) rather than the species of inorganic arsenic. The actual species of inorganic arsenic are assumed to be those predicted by a geochemical equilibrium model.

11.0 QUALITY CONTROL REQUIREMENTS

All contaminant analyses performed in this study will be performed in conjunction with the standard QC elements described in the EPA 600 and 1600 series methods. In developing these methods, EPA sought scientific and technical advice from many sources, including EPA's Science Advisory Board, scientists at EPA's environmental research laboratories, scientists in industry and academia, and scientists, managers, and legal staff at EPA Headquarters. The results of discussions held among these groups was the standardized QA/QC approach that is an integral part of the 600- and 1600- series methods. Over the years, these QA/QC requirements have been refined to reflect improvements in environmental science and policy. The most current version of these QC elements include the following:

Procedural requirements:
- Use of pure and traceable reference standards
- Demonstration of instrument calibration and system performance.
- Periodic calibration verification.

Sensitivity requirement:
- Verification that the laboratory can achieve required MDLs and MLs

Precision and accuracy requirements:
- Analysis of initial precision and recovery (IPR) samples to demonstrate the laboratory can achieve precise and accurate results with the method prior to use on field samples. IPR samples consist of a reference matrix spiked to a known level with the target analytes. The reference matrix is chosen so that it matches the field samples (e.g., corn oil or powdered eggs for fish samples). Accuracy is measured by the average recovery in the replicate IPR samples; precision is measured by relative standard deviation (i.e., RSD = standard deviation/mean) of the measured levels in the IPR samples.

- Analysis of ongoing precision and recovery (OPR) samples to demonstrate continued laboratory performance with the method. OPR samples are prepared in the same manner as the IPR samples.
- Analysis of certified reference materials (CRM), where available.
- Recovery of surrogate or labeled compounds, where available, spiked into the sample to assess the effect of matrix interferences on compound identification and quantitation.
- Duplicate matrix spike analyses (MS/MSD) to assess the effect of matrix interferences in non-isotope dilution methods
- Calculation and monitoring of accuracy and precision using results from IPR, OPR and CRM samples.
- Absolute and relative retention time precision (for chromatographic analyses).
- Analysis of blanks to demonstrate freedom from contamination.

All the methods to be used in this study will contain procedures for calculating each of the required method performance statistics. To ensure acceptable analytical performance, method performance criteria for new or modified methods will be established through validation studies on fish matrices. These validation studies will be completed prior to the analytical phase of the National Fish Tissue Study such that the performance criteria will be available to the laboratories before actual field samples need to be analyzed. Table 2 summarizes the method performance statistics and how these will be used to control data quality for this study.

Table 2. Method performance criteria

Statistic	Description	Required frequency
Method Detection Limit (MDL) and Minimum Level (ML)	To be obtained following procedures described in 40 CFR part 136 Appendix B.	All laboratories participating in the study will be required to do one MDL study per year on a fish tissue matrix before the analysis of actual field samples. The resulting MDL must support the ML stated in the method. The lowest standard used to calibrate the instrument must be at or below the ML.
IPR recovery IPR relative standard deviation (RSD)	Average measured concentration or recovery of at least 4 replicate IPR samples Standard deviation divided by the average measured concentration of at least 4 replicate IPR samples.	All laboratories participating in the study will be required to do one IPR study per year on a reference matrix suitable for fish tissue once before the analysis of actual field samples. The IPR recovery and RSD must be within the acceptable range given in the method.
Labeled or surrogate compound recovery	Recovery of labeled and surrogate compounds spiked into all samples; only applicable to some methods.	Labeled and surrogate standards are spiked into every sample analyzed. Recoveries must be within the acceptable range given in the method.
OPR recovery	Measured concentration or recovery of an OPR sample (prepared in the same manner as an IPR sample).	One typically required per analytical batch (specific frequency provided in the methods). Recovery must be within the acceptable range given in the method.
Matrix spike (MS) recovery Matrix spike (MS) precision	Average recovery from duplicate spiked field samples (MS/MSD) RPD between measured concentration in duplicate spiked field samples (MS/MSD)	Laboratories will be required to spike in duplicate 10% of each batch of samples received for analysis. Laboratories will determine specific samples to spike. Average MS recoveries and RPDs must be within the acceptable range given in the method.
Analytical precision (includes sample homogenization, compositing, and aliquotting)	RPD between duplicate analyses of a composite sample.	Laboratories will be required to analyze in duplicate 5% of the composite samples (to be specified by SCC). The RPD of the duplicate measurements must be less than 50% for values greater than 5 times the MDL, and must be less than 100% for values less than 5 times the MDL.

The analytical variability in actual field samples will be assessed by the analysis of blind composite duplicates on 5% of the samples (see Section 4.2.1).

12.0 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

Each laboratory participating in this study will be responsible for testing and inspecting the equipment used in this study. The laboratories also will be responsible for implementing preventative and corrective maintenance necessary to produce precise and accurate data that meets the measurement quality objectives listed in this QAPP. Specific requirements for maintaining the equipment at each laboratory will be documented in the laboratory QA plans used during the course of this study. Specific records of preventative maintenance, problems, and corrective actions will be documented by each laboratory in instrument log-books maintained on-site in the laboratory. These logbooks will be periodically reviewed by a laboratory manager/supervisor and will be available to an external audit team upon request.

13.0 INSTRUMENT CALIBRATION AND FREQUENCY

All laboratories supporting this study will be required to calibrate instruments used in the study prior to analysis of field samples and to periodically verify calibration during the course of the study. Calibration standards used by the laboratories will need to be certified as to purity, concentration, and authenticity, or prepared from materials of known purity and composition. Detailed instrument calibration procedures will be specified in each of the analytical methods or laboratory contracts.

All methods employed in this study require a multi-point calibration prior to use of the instrument for analysis of field and QC samples. The frequency of this initial, multi-point calibration varies across methods due to variations in instrument stability and calibration procedures. While some methods, such as those that employ atomic absorption (AA) spectroscopy, require daily calibration of the instrument, other methods, such as those that employ GC/MS, require the instrument to be calibrated only if the calibration verification standard fails to meet pre-defined acceptance criteria. All methods require the laboratory to verify instrument calibration at least once per working shift during which samples are analyzed. Because the stability of instruments vary by instrument type, the length of an allowable working shift varies and is specified in each method.

14.0 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONSUMABLES

The laboratories participating in this study will not be providing supplies or consumables to EPA. Contract laboratories that consume materials (e.g., chemical standards, equipment) during the course of sample preparation and analysis will be required to adhere to the inspection and acceptance requirements outlined in the contracts and their approved Quality Assurance Project Plans. Each contract will stipulate that the laboratory have a comprehensive QA program in place and operating at all times during the performance of their contract, and that in performing laboratory work for this study, they shall adhere to the requirements in the analytical methods specified for the study, to *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations* and the general laboratory procedures specified in the *Handbook for Analytical Quality Control in Water and Wastewater* (EPA-600-4-79-019). Cumulatively, these sources provide guidelines concerning laboratory inspection and acceptance of chemical standards.

15.0 REQUIREMENTS FOR ACQUISITION OF NON-DIRECT MEASUREMENT DATA

The analytical phase of this study will not involve the collection of data obtained from non-measurement sources such as computer databases, spreadsheets and programs, and literature files.

16.0 DATA MANAGEMENT

Data management practices employed in this study will be based on standard data management practices used by EAD's Analytical Methods Staff (AMS). The data management (i.e., sample tracking, data tracking, data inspection, data quality assessment, database development) procedures employed by EAD are routinely used to support the development of effluent limitation guidelines and standards and have regularly been applied to other technical studies. These procedures are being employed because they are effective, efficient, and have successfully withstood repeated internal and external audits, including internal review by the Quality Assurance Division, public review and comment, judicial challenge, and the Government Accounting Office audit. These procedures, as implemented for the National Fish Tissue Study, are summarized below.

16.1 Laboratory Data Management

Laboratory data management procedures will be detailed in individual contracts for all laboratories selected to participate in the National Fish Tissue Study. Briefly, they will include the following:

- Each laboratory participating in this study will be required to maintain all records and documentation associated with the preparation and analysis of Lake Fish Study samples for a minimum period of five years after completion of the study.
- To facilitate data tracking, each laboratory will be required to use EPA-assigned episode and sample numbers when reporting results.
- All results of sample analyses, labeled and native standards, surrogate compounds, spike compounds, and blanks must be reported on hard copy and on electronic media.
- All required reports and documentation, including chromatograms and mass spectra, must be sequentially paginated and clearly labeled with the laboratory name, contract number, episode number, and associated EPA sample numbers. Any diskettes, or other electronic media submitted must be similarly labeled.
- Unless otherwise approved, the laboratories will use the hard copy reporting forms and automated data reporting formats specified in the contract when reporting data.
- Each of the laboratories will adhere to a comprehensive data management plan that is consistent with the principles set forth in *Good Automated Laboratory Practices*, EPA Office of Administration and Resources Management, October 10, 1995. This data management plan must be in place and in use at all times during performance of the contracts.

16.2 SCC Data Management

Data management procedures employed by SCC will include the use of 1) an automated scheduling and tracking system to effectively manage data review and database development activities, 2) standardized data review guidelines to promote consistency in data quality audits across reviewers and over time, 3) a multi-stage data review process designed to maximize the amount of useable data

generated in each study, and 4) a standardized database development process that facilitates rapid development of a database with at least 99.9% accuracy.

The automated sample scheduling and tracking system will facilitate development of up-to-date information concerning work in progress, projected delivery dates, and notice of any problems encountered with laboratory analyses or data turnaround times. To ensure that this information is as complete and accurate as possible, entries will be made into the tracking system at each stage of the sample-to-data sequence.

Standardized data review guidelines will be used in this study to facilitate rapid, consistent, accurate, and thorough data quality audits. Data review guidelines already have been developed and are in use for a variety of analyses performed under EPA EAD programs. These guidelines detail method-specific data review procedures for commonly used methods and more general procedures that can be applied to less frequently used methods. Where appropriate, SCC will modify existing data review guidelines as necessary to reflect the methods, method modifications, and data quality objectives for the National Fish Tissue Study. Any modifications deemed to be necessary will be made in accordance with the *Quality Assurance Program Plan for the Environmental Protection Agency, Office of Water, Sample Control Center* (August 4, 1993 or subsequent updates, if applicable).

Although each guideline will be written for a specific method, technique, or group of analytes, all guidelines will specify a general five-stage review process that will ensure data are in proper format, are complete, are contractually compliant, and are usable. SCC chemists will use this multi-stage process to verify the quality of each laboratory submission under the National Fish Tissue Study. If an error is detected in any stage of the review, SCC staff will initiate corrective action procedures to obtain the maximum amount of usable data from the study. These actions may serve to obtain missing data, correct typographical or transcription errors on data reporting forms, or initiate reanalysis of field or QC samples that do not meet the performance criteria for this study.

Concurrent with the performance of data quality audits, SCC staff will begin developing a database of combined field and analytical results. At a minimum, this database will be formatted in a manner that is consistent with EAD effluent guidelines databases with modifications in the format necessary to integrate field data. The database also will be compatible with STORET; data will stored on a stand-alone PC version of STORET during the study and delivered to EPA upon study completion or at requested intervals. Each record in the database will contain information pertaining to both a "field sample" and to an "analytical sample". At a minimum, each record should include fields containing the following information:

- Five-digit EPA sample number assigned by SCC;
- 10-digit composite sample identification number assigned by field teams;
- Sample type (indicates the type of sample, whether it was a composite, duplicate analysis of a composite, matrix spike, etc);
- Species;
- Length of fish;
- Method of collection (active or passive);
- Sample collection date;
- Lake from which fish samples in composite were collected;
- Year fish samples in composite were collected (1999, 2000, 2001, 2002);

- Ecological group (predator or bottom-dwelling);
- EPA sample number of associated duplicate composite, if available;
- Analyte levels; and
- Lipid content measurements.

The data structure listed above for the integrated field and analytical database and the field database (Section 16.1) will allow data users and reviewers to:

(1) Look up individual fish sample data in the database for a given composite sample number.
(2) Extract analytical data from a given lake from the database.
(3) Extract fish sample data from a given lake from the database.
(4) Extract data from duplicate composite analyses to assess analytical variability.
(5) Extract data from duplicate composites (i.e., two composites collected from a lake within the same sampling period) to assess population and analytical variability.

As with the data quality audits, a multi-stage process of inspections and corrective actions will be used to facilitate timely, efficient construction of databases that are least 99.9% accurate. The database development process will begin with a completeness check to verify the laboratory has submitted a diskette and that the diskette contains all data in an appropriate format. If deficiencies are found, appropriate corrective action measures will be initiated. After problems have been identified and resolved, the SCC Database Administrator will prepare a "QC Check Report" that displays the results submitted by the laboratory. The SCC chemist responsible for performing the data quality audit will review this QC Check Report to verify that the electronic data accurately reflect the hard copy submission. Accuracy will be confirmed by spot checking at least 10% of all results that were downloaded directly from an analytical instrument in the laboratory and by performing a 100% QC check of data that were manually entered by the laboratory or SCC. Corrective actions will be taken as needed to resolve deficiencies. Following completion of the data quality audit, the SCC chemist and the Database Administrator will modify the database to reflect data usability determinations. A report, generated to reflect the modified database, will then be reviewed by the SCC chemist to verify database accuracy before submission to EPA.

17.0 ASSESSMENTS AND RESPONSE ACTIONS

Each laboratory contract prepared to support this study will stipulate that the laboratory have a comprehensive QA program in place and operating at all times during the performance of their contract, and that in performing laboratory work for this study, they shall adhere to the requirements in the analytical methods specified for the study, to *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations*, the general laboratory procedures specified in the *Handbook for Analytical Quality Control in Water and Wastewater* (EPA-600-4-79-019), and the data management principles set forth in *EPA 2185- Good Automated Laboratory Practices*, EPA Office of Administration and Resources Management, August 10, 1995. Cumulatively, these sources describe assessment and response actions that should be implemented within the laboratory (e.g., bench level review of results and calculations, independent surveillance by a QAO, periodic in-house audits, etc.).

Sections 17.1 - 17.7 describe other types of assessment activities and corresponding response actions identified to ensure that data gathering activities in the National Fish Tissue Study are conducted as prescribed and that the measurement quality objectives established in this QAPP and the performance criteria defined for the study are met. These activities are summarized in Table 3.

17.1 Surveillance

An SCC Sample Scheduling Coordinator will been assigned to facilitate sample scheduling and to track the location of samples and data throughout the study. During sample collection, the Sample Scheduling Coordinator will maintain communication with field sampling coordinators and teams to identify and notify the recipient Sample Preparation Laboratory of any delays or anticipated changes to the sampling plan. In the event these delays or changes impact the laboratory's contract or EPA schedules, the Sample Scheduling Coordinator will notify the EPA Analytical Project Manager and work with EPA, the sampling teams, and other SCC staff to identify and implement an appropriate solution.

When samples are shipped to the Sample Preparation Laboratory or the analytical laboratories, the Sample Scheduling Coordinator will contact designated laboratory staff to notify them of the forthcoming shipment(s) and request that they contact SCC if the shipments do not arrive intact as scheduled. Within 24 hours of scheduled sample receipt, the Sample Scheduling Coordinator will contact the laboratory to verify that the samples arrived in good condition, and if problems are noted, will work with the laboratory, the sampling team, and EPA to resolve the problem as quickly as possible to minimize data integrity problems.

The Sample Scheduling Coordinator also will communicate periodically with laboratory staff to monitor the progress of sample preparation, analysis, and data reporting. If technical problems are encountered during sample preparation and analysis, the Sample Scheduling Coordinator will discuss the situation with SCC Study Coordinator. If warranted, the Study Coordinator will identify a technical expert within SCC to assist in resolving the problem, work with the Scheduling Coordinator, the technical expert, laboratory staff, and EPA to identify and implement a solution to the problem. If laboratories fail to deliver data on time, or if the laboratories notify SCC of anticipated reporting delays, the Sample Scheduling Coordinator will notify the Study Coordinator and the EPA Analytical Project Manager of the situation. To the extent possible, the Study Coordinator will adjust schedules and shift resources within SCC as necessary to minimize the impact of laboratory delays on EPA schedules. The Study Coordinator also will immediately notify the Analytical Project Manager of any laboratory delays that are anticipated to impact EPA schedules.

Finally, the SCC Study Coordinator will monitor the progress of the data quality audits (data reviews) and database development to ensure that each laboratory data submission is reviewed in a timely manner. In the event that dedicated staff are not able to meet EPA schedules, the SCC Study Coordinator will work with the SCC Project Manager to identify additional resources who are qualified and capable of reviewing the data in a timely manner. If such resources cannot be identified, and if training new employees is not feasible, the SCC Project Manager will meet with the EPA Analytical Project Manager to discuss an appropriate solution.

Table 3 - Assessment and Response Actions

Assessment Measure	Definition	Frequency	Responsible Party	Rationale
Surveillance	Continual or frequent monitoring and verification of the status of an entity and the analysis of records to ensure that specified requirements are being fulfilled	Throughout sample preparation, laboratory analysis, and data review procedures	SCC Sample Sched. & Study Coordinators	Identify and correct analytical problems as soon as they occur to minimize delays; and to notify data users of potential delays as early as possible
Peer Review	A documented critical review of work. Conducted by qualified individuals who are independent, but technically equivalent of those who performed the work.	Performed on 5% of data audits conducted by SCC data reviewers and 100% of data review narratives prepared by SCC data reviewers	SCC data reviewers not responsible for original data review	Ensure that activities are technically adequate, competently performed, properly documented, and satisfy established technical and quality requirements.
Quality System Audit	Qualitative assessment of a data collection operation and/or organization to establish whether the prevailing quality management structure, policies, practices, and procedures are adequate for ensuring that the type and quality of data needed are obtained.	Not scheduled during this study	Not applicable	Standard EAD/SCC procedures will be used for gathering laboratory data in this study. Such procedures already have been approved following MSRs conducted by GAO and by EPA ORD.
Readiness Review	A systematic documented review of the readiness for the start-up or continued use of a facility, process or activity. Typically conducted before proceeding beyond project milestones and prior to initiation of a major phase of work.	Prior to each laboratory's analysis of field samples collected during each year of the study.	Lab staff and SCC data reviewers	Verify that laboratory is capable of producing precise and accurate results with the method(s) they will use during the study
Technical Systems Audit	A thorough, systematic, on-site, qualitative audit of facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a system.	As needed basis only. TSAs are not required for this study unless specific concerns are raised through discussions with laboratory staff or during other data assessment activities.	If TSAs are deemed necessary, they will be performed by EPA Project Manager and/or EPA QAO, and SCC staff	Ability of each laboratory to adequately analyze and report data will be assessed prior to analysis and continually throughout analyses via other QA/QC measures described in this QAPP.
Audit of Data Quality	Systematic and independent examination to determine if quality activities and related results comply with planned arrangements and whether these arrangements are implemented effectively and are suitable to achieve objectives.	100% of laboratory data packages submitted	SCC Data Reviewers	To verify that all data collected meet MQOs established for this study.
Data Quality Assessment	Statistical and scientific evaluation of the data set to determine the validity and performance of the data collection design and statistical test, and to determine the adequacy of the data set for its intended use.	Upon completion of data review and database development	SCC Staff and EPA Data Users	Evaluate overall accuracy and quality of the database, and identify trends in field and QC results.

17.2 Peer Review

All laboratory results and calculations will be reviewed by the laboratory manager prior to data submission. Any errors identified during this peer review will be returned to the analyst for correction prior to submission of the data package. Following correction of the errors, the Laboratory Manager will verify that the final package is complete and compliant with the contract, and will sign each data submission to certify that s/he has reviewed the package and determined it to be in compliance with the terms and conditions of the contract.

Peer reviews also will be performed within SCC to verify that the data quality audits are being performed consistently over time and across peer reviewers, that the audit findings are technically correct, and that the audits are being performed in accordance with this QAPP. These peer reviews of the SCC data quality audit process will be performed on at least 5% of the data packages received in this study. Peer reviewers will be charged with evaluating the completeness of the original data review, the technical accuracy of the reviewers findings, and the technical accuracy of the analytical database developed to store results associated with the data package. The SCC Data Review Manager will be responsible for identifying and assigning qualified peer reviewers and for selecting packages to be peer reviewed. Qualified peer reviewers will include any staff members that have been trained in SCC data review procedures, that are experienced in reviewing data similar to those being reviewed, and are familiar with the requirements of the National Fish Tissue Study and this QAPP. Data packages will be selected for peer review in such a way as to maximize the number of data reviewers and types of data (e.g., pesticides, dioxins, mercury, etc) that are subjected to this peer review process. To the extent possible, these peer reviews will be performed after the primary data reviewer has drafted a written narrative describing the results of his/her audit, but before this narrative is submitted to EPA.

To ensure the findings of each data quality audit are documented in a consistent and technically accurate manner, SCC staff will peer review 100% of the data review summaries (narratives) prepared for this study. Each data review summary will be subjected to at least two levels of peer review, and each peer reviewer will be charged with evaluating the clarity, technical accuracy, and the grammatical quality of the data review summary.

17.3 Quality Systems Audit

All data gathering procedures routinely used by EAD's Analytical Methods Staff (AMS) will be applied to the data gathering activities associated with this study. These standard AMS procedures have been subjected to periodic Management Systems Reviews by external sources interested in assessing the overall quality of EAD's data collection operation. In every case, the external reviewers found AMS' data gathering process to be technically sound.

Because the data gathered in the National Fish Tissue Study will be collected in accordance with standard AMS protocols, and because these protocols have repeatedly withstood external reviews, EPA has concluded that a formal Management Systems Review focused on the National Fish Tissue Study is unnecessary.

17.4 Readiness Review

A readiness review of each laboratory's capability to produce precise and accurate results with the methods specified in this study will be performed before the laboratories are allowed to analyze field

samples collected during the study. As part of the readiness reviews, the laboratories will submit data demonstrating that they are capable of analyzing a known, reference matrix with the methods to be used in this study. In most cases, laboratories will meet this requirement by performing IPR tests. IPR tests consist of preparing four replicate aliquots that contain the target pollutants, analyzing these replicate aliquots with the specified method, and calculating the average percent recovery and standard deviation of the measured aliquots. If the average percent recovery and standard deviation meet pre-defined acceptance criteria, the laboratory is considered to be qualified, or ready, to perform the analyses.

On a case by case basis, EPA and SCC may decide to accept alternate data in lieu of IPR data for the readiness reviews. In such cases, the alternate data must provide as much information about laboratory readiness as would the IPR samples. Examples of acceptable non-IPR data that might be used for a readiness review include: performance evaluation (PE) sample data; ongoing QC data gathered over a period of time, or MDL study data.

Readiness reviews will be performed by SCC data reviewers, who will document and forward their findings to the SCC Study Coordinator. If problems are identified during these reviews, the SCC Data Reviewer(s) and Study Coordinator will work with the laboratory, to the extent possible, to resolve the problem. If the problem cannot be resolved within the time frame required by EPA or within the scope of the laboratory's existing contract, the SCC Study Coordinator will notify the EPA Analytical Project Manager immediately.

17.5 Technical Systems Audit

All laboratory contracts will require that laboratories participating in this study be prepared for and willing to undergo an on-site, or technical systems, audit of its facilities, equipment, staff, and sample analysis, training, record keeping, data validation, data management, and data reporting procedures. Audits for individual laboratories participating in this study will be conducted only if the results of the readiness reviews, data quality audits, and surveillance suggest serious or chronic laboratory problems that warrant on-site examinations and discussion with laboratory personnel. If such an audit is determined to be necessary, a standardized audit checklist will be used to facilitate an audit walkthrough and document audit findings. Audit participants will include the EPA Analytical Project Manager or the EPA Quality Assurance Manager (or a qualified EPA staff member designated by the EPA QAM) and an SCC staff member experienced in conducting laboratory audits. One audit team member will be responsible for leading the audit and conducting a post-audit debriefing to convey significant findings to laboratory staff at the conclusion of the audit. The other audit team member will be responsible for gathering pre-audit documentation of problems that necessitated the audit, customizing the audit checklist as necessary to ensure that those problems are addressed during the audit, documenting audit findings on the audit checklist during the audit, and drafting a formal report of audit findings for review by EPA.

17.6 Data Quality Audits

Every laboratory data package submitted under this study will be subjected to a data quality audit. These data quality audits will be performed by qualified SCC data review staff who have been trained in procedures for performing data quality audits and who are familiar with the laboratory methods used to prepare the data packages. These data quality audits will be performed using a multi-stage review process designed to identify and correct data deficiencies as early as possible in order to maximize the amount of usable data generated during this study.

17.7 Data Quality Assessment

Upon completion of each data quality audit, the SCC Data Reviewer will work with SCC's database development staff to create an analytical database that contains all field sample results from the National Fish Tissue Study (see Section 16.3).

At selected intervals and upon completion of the study, SCC's database development staff will perform statistical analyses to verify the accuracy of the database. The statistical procedures will be directed at evaluating the overall quality of the database against data quality objectives established for the study, and in identifying trends in field and QC results obtained during the study. SCC staff will document their findings and recommendations concerning this data quality assessment in a written report to EPA.

18.0 REPORTS TO MANAGEMENT

Following completion of each data quality audit and assessment, SCC chemists will prepare and submit written reports, in narrative format, that describe data quality limitations and SCC recommendations concerning data use.

To facilitate sample and data tracking during the course of the National Fish Tissue Study, SCC also will prepare a monthly status report that provides a complete listing of the Episodes scheduled, the analyses required under each Episode, the laboratory associated with each analysis type, the date of sample receipt at the laboratory, the date of data receipt at SCC, the SCC data review completion date, and the SCC database completion date. This report will enable the Analytical Project Manager to quickly determine the status of individual National Fish Tissue Study components. This monthly status report also will be used by the EPA Analytical Project Manager and other EPA staff to facilitate decisions regarding the study and to inform senior EPA managers of the project status.

Upon request, SCC also will provide a weekly report that describes the status of all current sampling, analysis, and data review activities, and periodic database status reports that provide up-to-date information concerning database developments that occurred since distribution of previous reports.

19.0 DATA REVIEW, VALIDATION, AND VERIFICATION

Criteria for acceptance:

A multi-stage data review process, as summarized in Section 16 and detailed below, will be used to evaluate the quality of all data submitted in the National Fish Tissue Study. Acceptance criteria against which data will be evaluated will include 1) study performance criteria and MQOs detailed in this and affiliated QAPPs, 2) applicable QC acceptance criteria outlined in the methods, and 3) best professional judgement (BPJ) of SCC chemists responsible for performing data quality assessments. The goal of this data review process will be to maximize the amount of useable data gathered in the study. This will be accomplished by 1) performing data reviews promptly so that corrective actions may be taken wherever possible, and 2) considering data quality failures in light of the entire analytical sequence rather than as isolated events.

Process:

In the first stage of the data review process, SCC chemists will perform a "Data Completeness Check" in which all elements in each laboratory submission will be evaluated to verify that results for all specified samples are provided, that data are reported in the correct format, and that all relevant information, such as preparation and analysis logs, are included in the data package. Corrective action procedures will be initiated if deficiencies are noted.

The second stage of the data review process will focus on an "Instrument Performance Check" in which the SCC chemists will verify that calibrations, calibration verifications, standards, and calibration blanks were analyzed at the appropriate frequency and met method or study performance specifications. If errors are noted at this stage, corrective action procedures will be initiated immediately.

Stage three of the data review process will focus on a "Laboratory Performance Check" in which SCC staff will verify that the laboratory correctly performed the required analytical procedures and was able to demonstrate a high level of precision and accuracy. This stage includes evaluation of QC elements such as the IPR and OPR tests, preparation and laboratory blanks, and reference standards. Corrective action procedures will be initiated with the laboratories to resolve any deficiencies identified.

In stage four of the data review process, the SCC chemist will perform a "Method/Matrix Performance Check" to discern whether any QC failures are a result of laboratory performance or difficulties with the method or sample matrix. Data evaluated in this stage will include matrix spike, matrix spike duplicate, duplicate sample, labeled compound, and surrogate spike results. The SCC chemist also will verify that proper sample dilutions were performed and that necessary sample cleanup steps were taken. If problems are encountered, the SCC chemist will immediately implement corrective actions.

Reconciliation with user requirements:

Finally, SCC will perform a "Data Quality and Usability Assessment" in which the overall quality of data is evaluated against the performance criteria and MQOs detailed in this QAPP. As noted above, this assessment will strive to maximize use of data gathered in this study based on performance criteria established for this study. This will be accomplished by evaluating the overall quality of a particular data set rather than focusing on individual QC failures. Results of this assessment will be documented in written data review narratives that SCC will submit to EPA. To expedite the process, these narratives will follow a standardized format and, wherever possible, utilize standardized language to communicate data limitations and SCC recommendations concerning data quality.

The EPA Study Manager, EPA QA officer, and other appropriate EPA representatives will utilize the SCC-generated data review narratives to make final data usability determinations regarding each set of sample results.

20.0 REFERENCES

(1) U.S. Environmental Protection Agency (USEPA). 1992. National Study of Chemical Residues in Fish. U.S. Environmental Protection Agency, Office of Science and Technology, Washington, D.C. EPA 823-R-92-008.

(2) U.S. Environmental Protection Agency (USEPA). *Study design document*. undated.

(3) U.S. Environmental Protection Agency (USEPA). *QAPP for Sample Collection Activities for a National Study of Chemical Residues in Lake Fish Tissue.* May 2000.

(4) *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations,* EPA QA/R-5, EPA Quality Assurance Division, Interim Final, November 1999.

(5) *EPA Guidance for Quality Assurance Project Plans, EPA QA/G-5,* EPA Office of Research and Development, Washington, D.C. 20460. EPA/600/R-98/018. February 1998.

(6) Appendix B, 40 CFR part 136

(7) U.S. Environmental Protection Agency (USEPA). 1997. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1: Fish Sampling and Analysis.* Second Edition. U.S. Environmental Protection Agency, Office of Water, Washington, D.C. EPA 823-B-97-009.

(8) Crecelius, E.A., N.S. Bloom, C.E. Cowan, and E.A. Jenne. 1986. "Speciation of Selenium and Arsenic in Natural Waters and Sediments, Volume 2: Arsenic Speciation." Final Report prepared for Electric Power Research Institute, Palo Alto, California by Battelle Pacific Northwest Laboratories, Richland, Washington.

(9) *Guide to Method Flexibility and Approval of EPA Water Methods*, EPA Office of Water, Engineering and Analysis Division (4303), Washington DC 20460. EPA-821-D-96-004. December 1996.