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Assessment and Remediation of Contaminated Sediments (ARCS) Program

Quality Assurance Program Plan

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ASSESSMENT AND REMEDIATION OF CONTAMINATED SEDIMENTS (ARCS) PROGRAM

QUALITY ASSURANCE PROGRAM PLAN

by

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The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), performed and funded the research decribed here. It has been peer reviewed by the Agency and approved as an EPA publication. Mention of corporation names, trade names, or commercial products does not constitute endorsement or recommendation for use.

It should be noted that the formal ARCS quality assurance program was initiated shortly after the EPA Environmental Monitoring and Systems Laboratory in Las Vegas (EMSL-LV), Nevada, with the assistance from Lockheed Environmental Systems & Technologies Company (LESAT) in Las Vegas, Nevada, under Contract No. 68-CO-0049, were identified and tasked with the implementation and daily operation of the ARCS QA program. EMSL-LV and LESAT first became involved in the ARCS QA program in January, 1990. However, the ARCS program was initiated in fiscal year 1989 and thus, some sample collection and experimentation had occurred prior to the establishment of a formal QA program by the Great Lakes National Program Office. Therefore, it should be noted that the following laboratories and their respective activities were performed using whatever QA/QC program was in place at the laboratory at the time the activity was undertaken:

1) U.S. Army Corps of Engineers - Buffalo, Chicago, and Detroit districts; sediment collection for Engineering/Technology workgroup from the Buffalo River, Saginaw River, and Indiana Harbor areas of concern,
2) Environmental Research Laboratory in Duluth, MN; sediment homogenization for the Engineering/Technology workgroup's samples from the Buffalo River, Saginaw River, and Indiana Harbor areas of concern, and Toxicity Identification Evaluation (TIE) sediment testing,
3) Large Lakes Research Station in Grosse Ile, MI; sediment sample collection from the Buffalo River, Saginaw River, and Indiana Harbor areas of concern for the Toxicity/Chemistry workgroup,
4) Battelle-Marine Sciences Laboratory in Sequim, WA; inorganic and organic chemistry of sediment, elutriate, and pore waters from the Buffalo River, Saginaw River, and Indiana Harbor areas of concern,
5) Michigan State University in East Lansing, MI; bioassay testing of samples from the Indiana Harbor area of concern,
6) National Fisheries Contaminant Research Center in Columbia, MO; bioassay testing in samples from the Buffalo River, Saginaw River, and Indiana Harbor areas of concern, and
7) Wright State University in Dayton, OH; bioassay testing in samples from the Buffalo River, Saginaw River, and Indiana Harbor areas of concern.

Since these activities were performed prior to the initiation of the formal ARCS QA program, the data generated by the laboratory will only be verified using the laboratory's QA program and <u>not</u> the ARCS QA program requirements. These differences will be clearly noted in the final data verification reports that will accompany the submitted and accepted databases from these laboratories. All sampling and laboratory efforts performed after the initiation of the formal ARCS QA program will be reviewed and subjected to the QA program presented in this document.

The correct citation of this document is:

Schumacher, B.A. 1993. Quality Assurance Program Plan for the Assessment and Remediation of Contaminated Sediments (ARCS) Program. EPA/600/R-xx/xxx. U.S. Environmental Protection Agency, Las Vegas, Nevada.

Foreword

On November 16, 1990, President George Bush signed into law the Great Lakes Critical Programs Act of 1990 (GLCPA). The GLCPA extends the ARCS program by one year and stipulates a number of activities to be conducted immediately. Since this QAPP was in preparation during the passage of the act, it does not necessarily reflect all the mandated changes in the Act.

Abstract

The Assessment and Remediation of Contaminated Sediments (ARCS) program is a congressionally mandated program, by the 1987 amendments to the Clean Water Act, Section 118(c)(3), designed to address the concern over the presence of polluted bottom sediments in the Great Lakes. ARCS is an integrated program for the development and testing of assessment and remedial action alternatives for contaminated sediments. Five areas of concern were specified in the Clean Water Act as requiring priority consideration in locating and conducting demonstration projects: Saginaw Bay, Michigan; Sheboygan Harbor, Wisconsin; Grand Calumet River, Indiana; Ashtabula River, Ohio; and Buffalo River, New York. It will be in these areas that the efforts of the ARCS program will be concentrated. While the ARCS program is not a cleanup program and will not solve the contaminated sediment problems at the five areas of concern, it will provide valuable experience, methods, and guidance that could be used by other programs to actually solve the contamination problem.

To accomplish the goals of contaminated sediment assessment and remediation, the Great Lakes National Program Office in Chicago, Illinois, will create two committees, one non-technical workgroup, and three technical workgroups. The two committees, namely, the Management Advisory Committee and the Activities Integration Committee, will be formed to provide oversight for the ARCS program and to develop the ARCS quality assurance program. The non-technical workgroup, the Communication/Liaison workgroup, will be responsible for the dissemination of up-to-date information regarding the ARCS program and related activities to elected officials, government agencies, and the interested public.

The three technical workgroups, namely, the Toxicity/Chemistry, the Engineering/Technology, and the Risk Assessment/Modeling workgroups, are responsible for the generation of data and subsequent documents to fulfill the goals of the ARCS program. The Toxicity/Chemistry workgroup will be responsible for developing and testing sediment assessment methods as well as producing maps of the contaminated sediments. The primary responsibilities of the Engineering/Technology workgroup will be to evaluate and test available removal and remedial technologies for contaminated sediments, to select promising new technologies for further testing, to demonstrate alternatives at priority consideration areas, and to estimate contaminant losses during remediation. The Risk Assessment/Modeling workgroup will be responsible for the evaluation of environmental and human health impacts resulting from contaminated sediments and the development of techniques for assessing the environmental impacts resulting from the implementation of remedial alternatives including the "no-action" alternative.

This document will address the design and implementation of the quality assurance program and the validation/verification of the resultant analytical database for the entire ARCS program. Individual sections addressing sampling strategy, field and laboratory operations, quality assurance objectives, quality assurance implementation, assessment and reporting of data quality, development of a quality assurance/quality control evaluation scale for historical databases, data quality assessment and reporting, as well as the database management system have been included to provide an overview of the ARCS quality assurance program.

This quality assurance management plan is submitted in partial fulfillment of contract number 68-CO-0049 by Lockheed Engineering and Sciences Company, Las Vegas, Nevada, to the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, under the sponsorship of the U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, Illinois.

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Acknowledgements

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Finally, the support of my technical monitor (when I was employed at Lockheed Engineering & Sciences Company), Wes Kinney, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory (Las Vegas, NV) and my ARCS project officer, Paul Horvatin, Great Lakes National Program Office (Chicago, IL) are gratefully acknowledged.

List of Acronyms

AA	atomic absorption spectrometry
AET	apparent effects threshold
AIC	Activities Integration Committee
AOC	area of concern
ARCS	Assessment and Remediation of Contaminated Sediments
ASTM	American Society for Testing and Materials in Philadelphia, Pennsylvania
AVS	acid volatile sulfides
BCD	base catalyzed destruction
B.E.S.T.	basic extraction sludge technology
BOM	Bureau of Mines in Salt Lake City, Utah
CDF	confined disposal facility
CF	critical fluids
CRM	certified reference material
CSO	combined sewer overflow
CSS	chemical solidification/stabilization
CVAA	cold vapor atomic absorption
CVAF	cold vapor atomic fluorescence
C/L	communication/liaison
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
DO	dissolved oxygen
DOC	dissolved organic carbon
DQO	data quality objective
EC	effective concentration
ECD	electron capture detector
EDTA	ethylenediamine tetraacetate
EMSL-LV	Environmental Monitoring Systems Laboratory at Las Vegas, Nevada
ERL-A	Environmental Research Laboratory in Athens, Georgia
ERL-D	Environmental Research Laboratory in Duluth, Minnesota
E/T	engineering/technology
FID	flame ionization detector
FPD	flame photoionization detection
FY	fiscal year
GC	gas chromatography
GFAA	graphite furnace atomic absorption
GLCPA	Great Lakes Critical Program Act
GLNPO	Great Lakes National Program Office in Chicago, Illinois
HPLC	high pressure liquid chromatography
ICP	inductively coupled plasma spectroscopy
IDL	instrument detection limit
IJC	International Joint Commission
INHS	Illinois Natural History Survey in Champaign, Illinois
LC	lethal concentration
LESAT	Lockheed Environmental Systems & Technology Company in Las Vegas, Nevada
LLRS	Large Lakes Research Station in Grosse Ile, Michigan
LOEL	lowest observable effect level
LTS	low temperature thermal stripping
MAC	Management Advisory Committee
MDL	method detection limit
MQO	measurement quality objective
MS	mass spectrometry
MSG	Michigan Sea Grant College Program
MSL	Marine Science Laboratory
MSU	Michigan State University in East Lansing, Michigan

List of Acronyms (cont.)

NAA	neutron activation analysis
NBS	National Bureau of Standards
NCC	National Computer Center
NFRC-GL	National Fisheries Research Center-Great Lakes in Ann Arbor, Michigan
NFCRC	National Fisheries Contaminant Research Center in Columbia, Missouri
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NOEL	no observable effect level
NYSDEC	New York State Department of Environmental Conservation in Albany, New York
ODES	Ocean Data Evaluation System
O&G	oil and grease
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PI	principal investigator
PID	photoionization detection
QA	quality assurance
QAPP	quality assurance program plan
QAPjP	quality assurance project plan
QC	quality control
QE	quality evaluation
RA/M	risk assessment/modeling
RAP	remedial action plan
RPD	relative percent difference
RREL	Risk Reduction Engineering Laboratory in Cincinnati, Ohio
RSD	relative standard deviation
SAIC	Science Applications International Corporation in Cincinnati, Ohio
SDL	system detection limit
SER	solvent extractable residue
SLT	serial leaching test
SOP	standard operating procedure
SQT	sediment quality triad
SRM	standard reference material
SUC-B	State University College of New York at Buffalo in Buffalo, New York
TCLP	toxicity characteristic leaching procedure
TIC	total inorganic carbon
TIE	toxicity identification evaluation
TOC	total organic carbon
TSS	total suspended solids
T/C	toxicity/chemistry
UCSB	University of California at Santa Barbara in Santa Barbara, California
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
WASP4	water quality analysis program
WES	Waterways Experiment Station in Vicksburg, Mississippi
WSU	Wright State University in Dayton, Ohio
XRF	X-ray fluorescence

Section 1
Introduction

1.1 Directives

The quality assurance policy of the United States Environmental Protection Agency (USEPA) requires that every monitoring and measurement project to have a written and approved quality assurance (QA) program and project plan (Costle, 1979a and 1979b). This requirement applies to all USEPA Regional Offices, Program Offices, USEPA Laboratories, and States and includes all monitoring and measurement efforts mandated or supported by USEPA through regulations, grants, contracts, or other formalized means not currently covered by regulation. The purpose of this Quality Assurance Program Plan (QAPP) is to specify the policies, organization, objectives, and the quality assurance and quality control (QC) activities needed to achieve the data quality requirements of the Assessment and Remediation of Contaminated Sediments (ARCS) program. These specifications are used to assess and control measurement errors that may enter the system at various phases of the project, e.g., during sediment sampling, preparation, and analysis.

1.2 Sources of Information

The USEPA Quality Assurance Management Staff guidelines (Stanley and Verner, 1985) state that the QAPP and Quality Assurance Project Plans (QAPjPs) should address in detail or by reference, each of the following 14 items:

1) project description,
2) project organization and responsibilities,
3) quality assurance objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability,
4) sampling procedures,
5) sampling custody,
6) calibration procedures and frequency,
7) analytical procedures and calibration,
8) data reduction, validation, and reporting,
9) internal quality control checks,
10) performance and system audits,
11) preventative maintenance procedures,
12) calculation of data quality indicators,
13) corrective actions, and
14) quality assurance/quality control reports to management.

Additionally, each QAPP and QAPjP must have a title page with provisions for approval signatures and a table of contents.

Each individual laboratory generating any form of data (i.e., field sampling, field descriptions, analytical results, sediment maps, etc.) for the ARCS program is required to prepare a QAPjP for their individual part of the ARCS program. These individual laboratory QAPjPs will address each of the 14 items in detail, however, a discussion of the fourteen points as they relate to the overall ARCS program will be presented in the rest of this document. Copies of the approved QAPjPs for the ARCS program will be maintained at the Great Lakes National Program Office (GLNPO) in Chicago, Illinois, and by the Environmental Monitoring and Systems Laboratory in Las Vegas, Nevada (EMSL-LV).

Section 2

Project Description

2.1 Project Overview

The 1987 amendments to the Clean Water Act, in Section 118(c)(3), authorizes the USEPA Great Lakes National Program Office to coordinate and conduct a 5-year study and demonstration project relating to the control and removal of toxic pollutants in the Great Lakes, with emphasis on removal of toxic pollutants from bottom sediments. Five areas were specified in the Clean Water Act as requiring priority consideration in locating and conducting demonstration projects: Saginaw Bay, Michigan; Sheboygan Harbor, Wisconsin; Grand Calumet River, Indiana; Ashtabula River, Ohio; and Buffalo River, New York (Figure 1). In response, GLNPO has initiated the Assessment and Remediation of Contaminated Sediments Program. ARCS is an integrated program for the development and testing of assessment and remedial action alternatives for contaminated sediments. Information from ARCS program activities will be used to guide the development of Remedial Action Plans (RAPs) for the 42 Great Lakes Areas of Concern (AOCs) as identified by the International Joint Commission (IJC), as well as Lakewide Management Plans (Figure 2). The ARCS program is scheduled to be performed from fiscal year (FY) 1988 through 1992.

While the Clean Water Act specifies that priority consideration should be given to the Ashtabula River, Buffalo River, Grand Calumet River, Saginaw Bay, and Sheboygan Harbor, it does not preclude considering other areas in the Great Lakes. The ARCS program will take advantage of ongoing sediment-related activities in these other locations where it would be beneficial. Some of the priority considerations areas are the sites of intensive work by other programs. Both the Ashtabula River and Sheboygan Harbor are being addressed under the USEPA Superfund Program. Rather than duplicate efforts in these areas, the ARCS program will follow these activities to utilize the information gained and will focus its resources only on factors that are not being addressed by the Superfund activities.

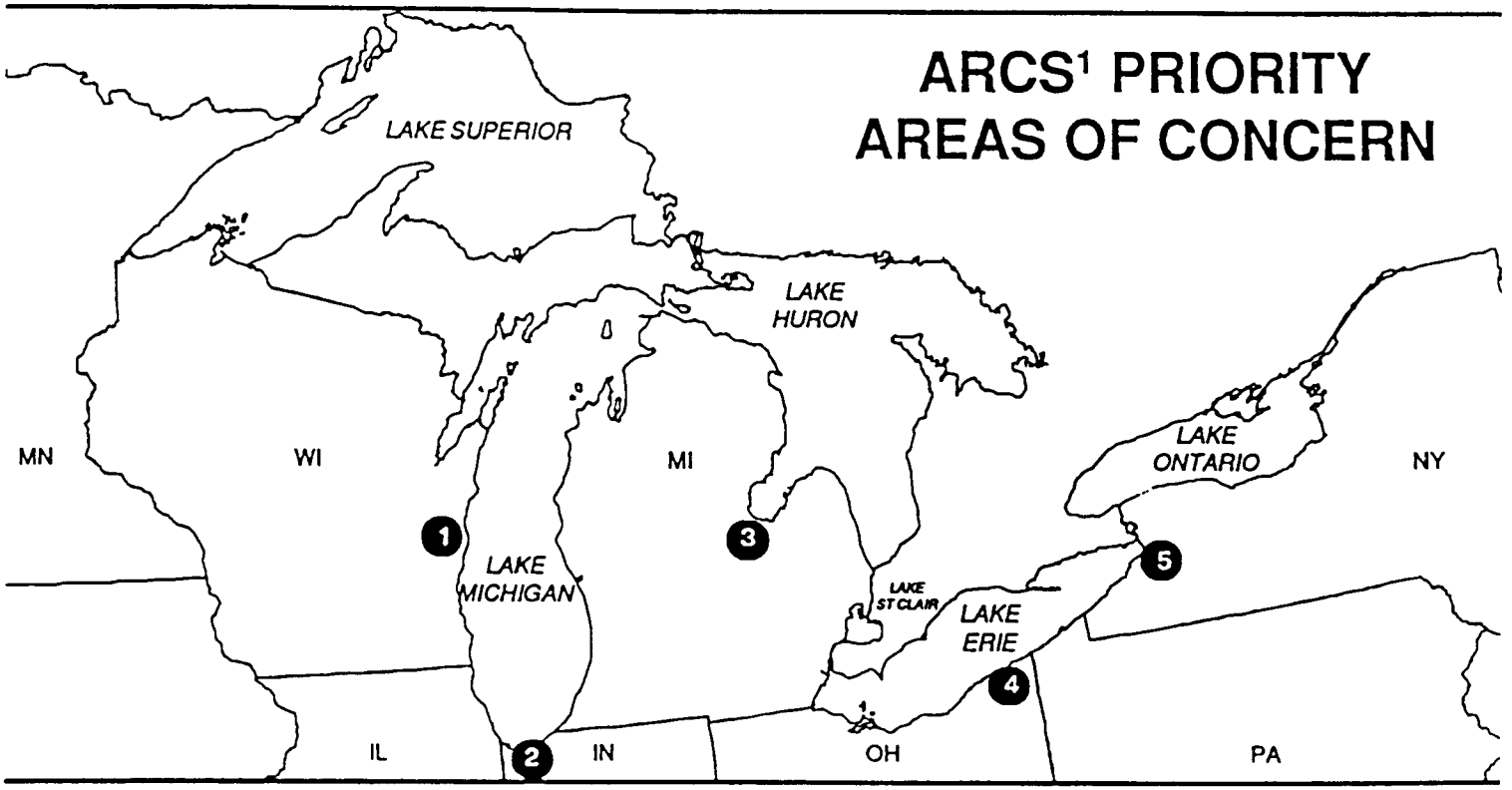

Figure 1. ARCS Priority Areas of Concern.

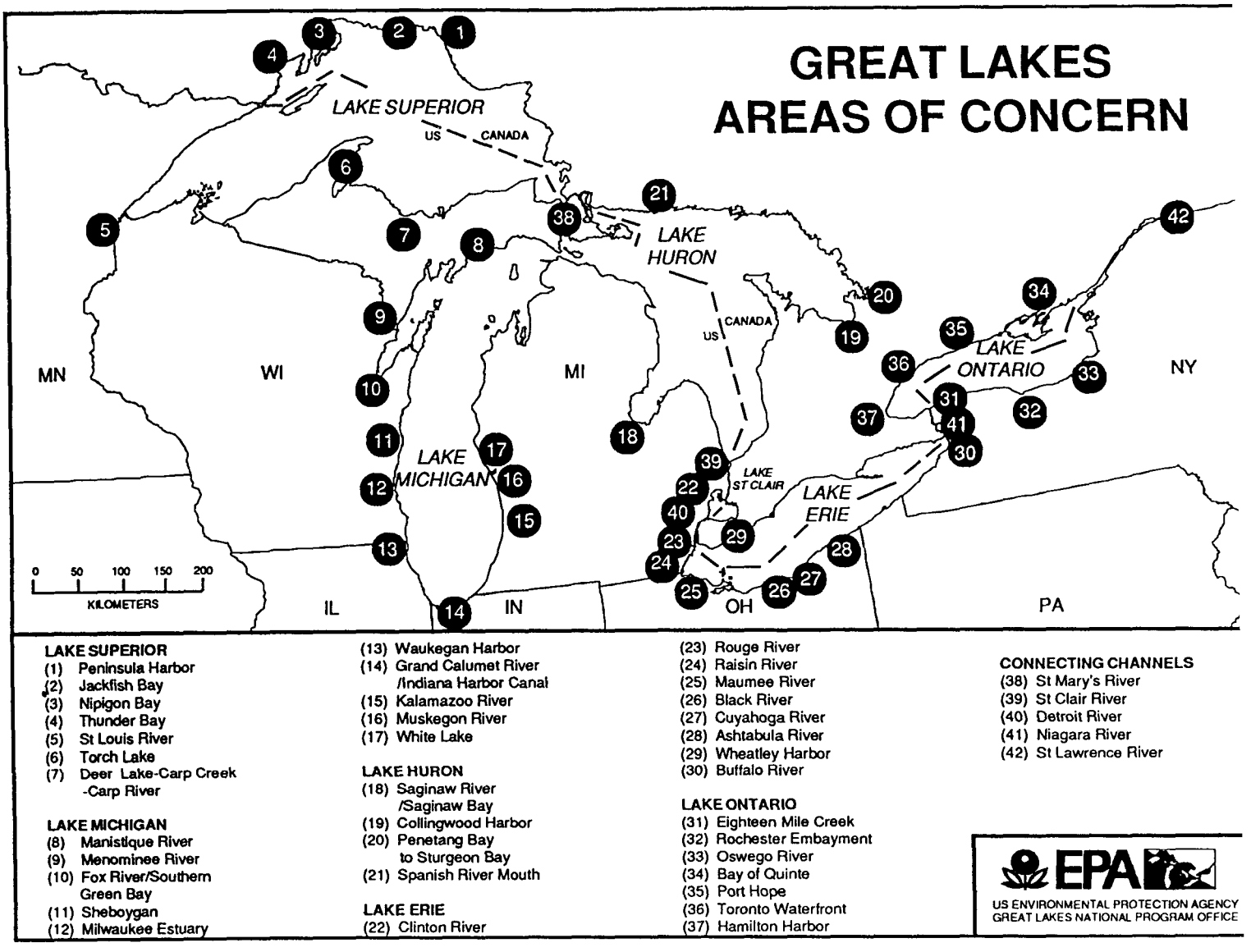

Figure 2. Areas of Concern on the Great Lakes as Identified by the IJC.

2.2 Project Objectives

The overall objectives of the ARCS program are to:

- assess the nature and extent of bottom sediment contamination at selected Great Lakes Areas of Concern,
- evaluate and demonstrate remedial options, including removal, immobilization, and advanced treatment technologies, as well as the "no action" alternative, and
- provide guidance on the assessment of contaminated sediment problems and the selection and implementation of necessary remedial actions in the Areas of Concern and other locations in the Great Lakes.

The primary aim of the ARCS program is to develop guidelines that can be used at sites throughout the Great Lakes. Site-specific factors at the five priority consideration areas will need to be considered in conducting assessments and choosing appropriate remedial alternatives for those locations. The varying characteristics at the five areas should provide a range of conditions applicable to other Great Lake sites. The five sites are to be viewed as case studies of the application of the procedures developed under the ARCS program.

Another important aim of the ARCS program is that the procedures developed and demonstrated be scientifically sound, and technologically and economically practical. The intent is to provide the environmental manager with methods for making cost-effective, environmentally sound decisions. As a result, application of existing techniques will be stressed over basic research into new technologies. Some developmental work will, however, be undertaken.

To completely assess the causes and effects of contaminated sediments and to fully evaluate the remedial options available, a mass balance of each of the AOCs, including quantification of contaminant loadings from point and non-point sources would be desirable. Unfortunately, such characterizations could cost several millions of dollars for each priority area. The ARCS program intends to use the available resources to develop a basic framework for site characterization. More in-depth evaluation may be performed if additional funds become available.

It is important to stress at the outset that the ARCS program is not a cleanup program and will not solve the contaminated sediment problems at the five priority consideration areas. The ARCS program will, however, provided valuable experience, methods, and guidance that could be used by other programs to actually solve the identified problems.

2.3 Project Organization

To accomplish the objectives of the ARCS program, two committees, one non-technical workgroup, and three technical workgroups will be established. The names of the individual workgroups and their basic responsibilities are as follows:

Management Advisory Committee: To advise the GLNPO Director on their perceptions of the overall progress of the ARCS program and to review annual work and funding plans for the ARCS program.

Activities Integration Committee: To oversee the ARCS program, including the technical activities of each of the workgroups, to develop and coordinate the QA/QC program, and to coordinate the data management activities of the ARCS program.

Toxicity/Chemistry Workgroup: To assess the current nature and extent of contaminated sediment problems by studying the chemical, physical, and biological characteristics of contaminated sediments and their biotic communities, to demonstrate cost-effective assessments techniques at the priority consideration areas that can be used at other Great Lakes AOCs, and to produce three-dimensional maps showing the distribution of contaminated sediments in the priority areas.

Risk Assessment/Modeling Workgroup: To assess the current and future hazards presented by the contaminated sediments to all biota (aquatic, terrestrial, and human) under the "no action" alternative and other remedial alternatives at the priority consideration areas, as well as to develop a ranking scheme for site comparison.

Engineering/Technology Workgroup: To evaluate and test available removal and remedial technologies for contaminated sediments, to select promising technologies for further testing, and to perform field demonstrations on as many of the promising technologies as possible.

Communication/Liaison Workgroup: To facilitate the flow of information from the technical workgroups and the overall ARCS program to the interested public and to provide feedback from the public to the ARCS program on needs, expectations, and perceived problems.

An organizational flow chart of the primary management structure is provided in Figure 3.

2.3.1 Management Advisory Committee

The Management Advisory Committee (MAC) is responsible for the overall guidance of the ARCS program. The MAC is chaired by the Director of GLNPO and composed of members from numerous participating agencies with interests in the Great Lakes region. The participating agencies include the U.S. Army Corp of Engineers (USACE), the U.S. Fish and Wildlife Service (USFWS), the National Oceanic and Atmospheric Administration (NOAA), other USEPA Headquarter Offices, USEPA

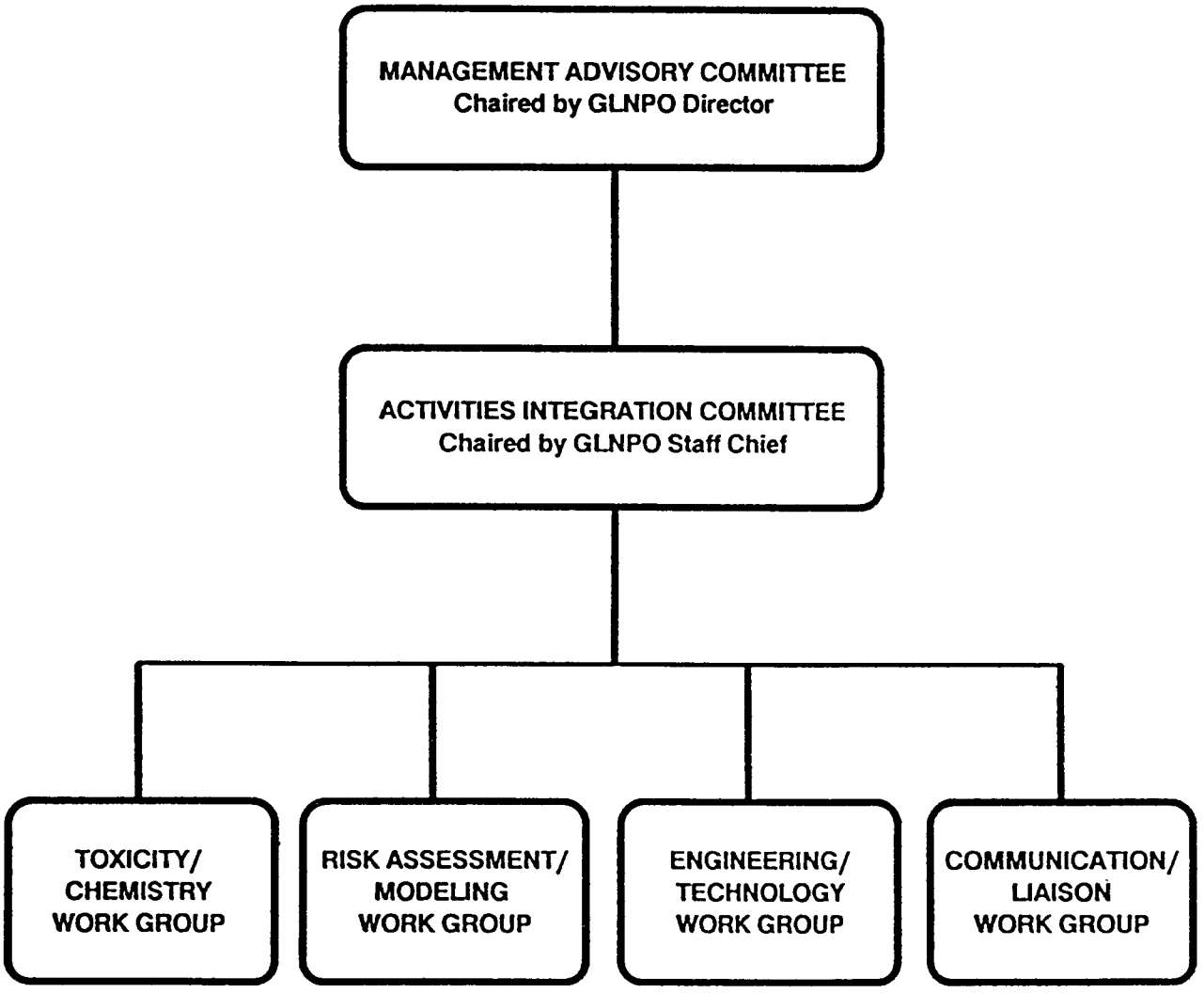

Figure 3. ARCS Management Structure.

Regions II, III, and V, Great Lakes State Agencies, universities, and public interest groups. Input by the MAC members may reflect both personal and professional opinions and/or the position of member's organization with respect to technical or policy issues. The advice of this committee will be used by the GLNPO Director to implement the recommendations of the AIC or amend them, as necessary. The MAC is also responsible for the review of ARCS work and funding plans to ensure the maximum utility of the products of the ARCS program.

2.3.2 Activities Integration Committee

The Activities Integration Committee (AIC) has three primary objectives which are as follows:

1. to coordinate and provide oversight of the technical aspects of the ARCS program including the activities of each of the workgroups,

2. to development and coordinate the QA/QC program for the ARCS program, and

3. to establish the ARCS data management program.

Coordination and oversight of the technical aspects of the ARCS program (objective 1) will be performed through a minimum of annual AIC workgroup meetings which include the chairpersons of each of the four workgroups listed above, the ARCS QA officer or representative, as well as, representatives from EMSL-LV, USEPA Region II, and USEPA Region V. As the ARCS program progresses and the decision making and data review processes become critical, more frequent meetings of the AIC will be held and weekly conference calls will be held to discuss important issues.

To achieve the second objective, the ARCS AIC will have overall oversight responsibility for the ARCS QA/QC program. The USEPA Environmental Monitoring and Systems Laboratory in Las Vegas, Nevada, with the assistance from Lockheed Engineering & Sciences Company, will be responsible for the implementation and daily operation of the ARCS QA/QC program. EMSL-LV and LESAT first became involved in the ARCS QA program in January, 1990. The primary tasks of EMSL-LV and LESAT are as follows:

1) assist in the development of program and project Data Quality Objectives (DQOs),
2) review QAPjPs submitted by the principal investigators (PI),
3) develop a laboratory and field audit program,
4) development of a quality assurance/quality control evaluation scale for historical datasets,
5) prepare a final QA report and appropriate sections/chapters for the case studies and guidance documents to be produced by the three technical workgroups, and
6) to act as an intermediate data repository for the ARCS program which includes database conversion, manipulation, and QA/QC validation.

Each of these tasks will be discussed in more detail in the following paragraphs.

Upon initial entry into the ARCS program in January 1990, a list of pertinent questions relating to the DQOs of the ARCS program will be developed and distributed to the ARCS management and each of the workgroups (excluding the Communication/Liaison workgroup since no measurement data will be generated by members of the workgroup) to satisfy task 1. The DQO questions will be formulated to stimulate the program participants into thinking about the objectives of the overall ARCS program and how their individual projects fit into the ARCS program. The questions will also

make the PIs think about what type of data will be generated, its particular relevance to the ARCS program, and how much error is allowable in their measurements (i.e., develop Measurement Quality Objectives - MQOs) such that their data would not compromise the overall objectives of the ARCS program.

The participating PIs are required to prepare QAPjPs for their projects to satisfy the DQOs and have their QAPjPs reviewed and approved by the QA staff at LESAT and EMSL-LV prior to the start of sample analyses (task 2). The signature/approval list for each QAPjP will include the PI, laboratory's QA officer, workgroup chair, ARCS QA officer, EMSL-LV QA officer, project officer, and ARCS program manager. The purpose of the QAPjP is to specify the policies, organization, objectives, and the quality assurance and quality control activities needed to achieve data of a "known and acceptable" quality for the ARCS program which meets the overall ARCS objectives. These specifications are used to assess and control measurement errors that may enter the system at various phases of the project, e.g., during sediment sampling, preparation, and analyses. Adherence to an overall Quality Assurance/Quality Control program is essential for a large, multi-participant program, such as ARCS, to ensure that the data collected by individual investigators will be comparable and congruous.

At EMSL-LV and LESAT, the QAPjP review process will consist of the following steps:

1) initial review by three scientists with at least one specializing in the area of quality assurance and one in the area of the principal type of analyses that are being performed (i.e., inorganic or organic chemistry, bioassay, etc.),
2) return of review comments to the PI for QAPjP revision, if necessary,
3) additional reviews by same three scientists to ensure appropriate modifications and clarifications have been made,
4) if acceptable, the QAPjP is then reviewed by the EMSL-LV QA officer for compliance with USEPA policy and for completeness of the document,
5) if approved by the EMSL-LV QA officer, the document is started through the approval signature cycle, and
6) upon receipt of the completely signed QAPjP, copies are made and distributed to the PI, ARCS program manager, workgroup chairs, EMSL-LV, and LESAT.

The review of the QAPjP will include checking for the inclusion and discussion of the sixteen general requirements for a QAPjP as specified by Stanley and Verner (1985). Specific checking for conformity of the laboratory and field specified MQOs to the ARCS-defined MQOs will also be performed. The review for the laboratory specified MQOs includes checking for acceptable instrument detection limits (IDLs), appropriate acceptance limits and frequency of use for accuracy, precision, blank, and spiked samples, suitable initial and ongoing calibration procedures, comparable analytical methodologies, satisfactory sample handling and preservation techniques, and the correct sample holding times for given sample types. Specific checking of the field activities in the ARCS program includes checking for proper and comparable field sampling techniques, sample handling procedures, sample preservation methods, and the appropriateness of instrumentation and QA/QC measures to be used during field sampling.

To ensure that the QAPjPs are being followed properly by the analytical laboratories, EMSL-LV will develop and perform a on-site system audit program (task 3) for both field and laboratory activities. In addition, EMSL-LV will periodically distribute pre-analysis audit samples and routine audit samples to participating laboratories at the request of GLNPO or the workgroup chairs. Audit samples of known toxicity or chemical concentration in an appropriate matrix (i.e., water or sediment/soil) will be prepared by the LESAT staff and distributed to the analytical laboratory as single-blind samples (i.e., the sample identity is known to the laboratory but the analyte concentrations are not).

EMSL-LV and LESAT will create and distribute to members of the Risk Assessment/Modeling workgroup and the ARCS management after their review, a quality assurance/quality control evaluation scale for historical datasets (task 4). The evaluation scale will help establish the confidence level the workgroup members can place in their resultant baseline hazard evaluations and may also be used to possibly explain some of the data outliers that may result from their modeling efforts. A point system in which the all essential QA/QC practices will be given numerical values by parameter group, such as inorganic metals, pesticides/PCBs, PAHs, etc., will be used. The historical data will then be rated on the sum total of various categories. Categories include accuracy, precision, spiked samples, detection limits, blank usage, calibration procedures, sampling technique, holding times, and other properties that might influence the integrity of the sample or the quality of the resultant data. If deficiencies in the received data are noted, additional QA/QC data will be requested from the analytical laboratory. If the deficiencies remain, flags will be attached to the parameter groupings. The flags will allow the data user to assess the value of the received data as is (actual rating) and the potential value of the data (assuming that if the flag indicates missing information, that the analytical laboratory properly and successfully performed the missing QA/QC measurements).

A final report for the ARCS program, the final QA report as listed for task 5, will be prepared by the ARCS QA Officer. The final QA report will provide discussions of the project organization, QA program (its successes and failures with possible explanations, where possible), audit program, data verification, an overview of the database structure and tracking, assessments of the success of the QA/QC protocols for detectability, accuracy, precision, representativeness, and comparability, as well as include a conclusion and recommendation section which addresses how well the program did from a QA/QC standpoint and provides guidance for future improvements on projects of a similar nature to those involved in the ARCS program. The final QA report will be initiated upon completion and receipt of the final database.

Appropriate sections or chapters for the case studies and guidance documents to be prepared by the three technical workgroups will be written by EMSL-LV and LESAT (task 5). For the case studies, the QA/QC sections to be provided by EMSL-LV and LESAT will include detailed descriptions of the QA/QC program that was applicable to all analyses performed by all laboratories whose data are used and presented in the particular case study. The guidance document chapter will include an idealized QA program, for the appropriate analyses, that will allow researchers, program planners, decision makers, etc., to be able to apply appropriate QA/QC measures during their future testing program(s).

EMSL-LV and LESAT will act as an intermediate data repository for the ARCS program (task 6). This responsibility will include the collection of all data from the analytical laboratories, creating computer programs to perform QA/QC checks on the data, conversion of the data from the received format to an Ocean Data Evaluation System (ODES) acceptable format, development of a cross-referencing system to track hardcopy data to its corresponding computer file, and to submit the final database on floppy disk to the ODES personnel for uploading onto the mainframe computer at the National Computer Center (NCC) in Research Triangle Park, North Carolina. A more complete discussion of the data management and the ODES system is provided in the section 9.0.

2.3.3 Toxicity/Chemistry Workgroup

The Toxicity/Chemistry (T/C) workgroup is responsible for developing and testing sediment assessment methods. An organizational chart displaying the laboratory name, laboratory location, the dominant type of analyses to be performed at the laboratory, and the principal investigator is presented in Figure 4. This workgroup will assess the nature and extent of contaminated sediments and their biotic communities. The workgroup will demonstrate effective assessment techniques for aquatic life at the priority consideration areas. Finally, it will use the information obtained to produce contamination maps of the priority areas.

To accomplish these goals, the following activities will be needed:

1) general characterization, sampling, and mapping of sediment deposits,
2) toxicity testing of sediment samples,
3) broader spectrum toxicity testing on a selected subset of sediment samples,
4) chemical analysis of sediment, sediment extracts, and fish tissue samples,
5) fish tumor and abnormality surveys,
6) fish bioaccumulation assays, and
7) mutagenicity testing of sediment extracts.

Upon completion of these tasks, the T/C workgroup will develop a guidance document that will indicate the most accurate and cost-effective methodologies which can be used to identify contaminated sediments under various contamination scenarios for future investigations.

In order to properly evaluate the nature and extent of sediment contamination in the AOCs, each of the areas will be characterized for physical, chemical, and biological parameters, including mapping the distribution of bottom sediments and sediment contaminants (goal 1). It is desirable to have information on the physical and spatial characteristics of the sediments and some basic indicator parameters to help select the stations that will be subjected to more intensive testing and characterization.

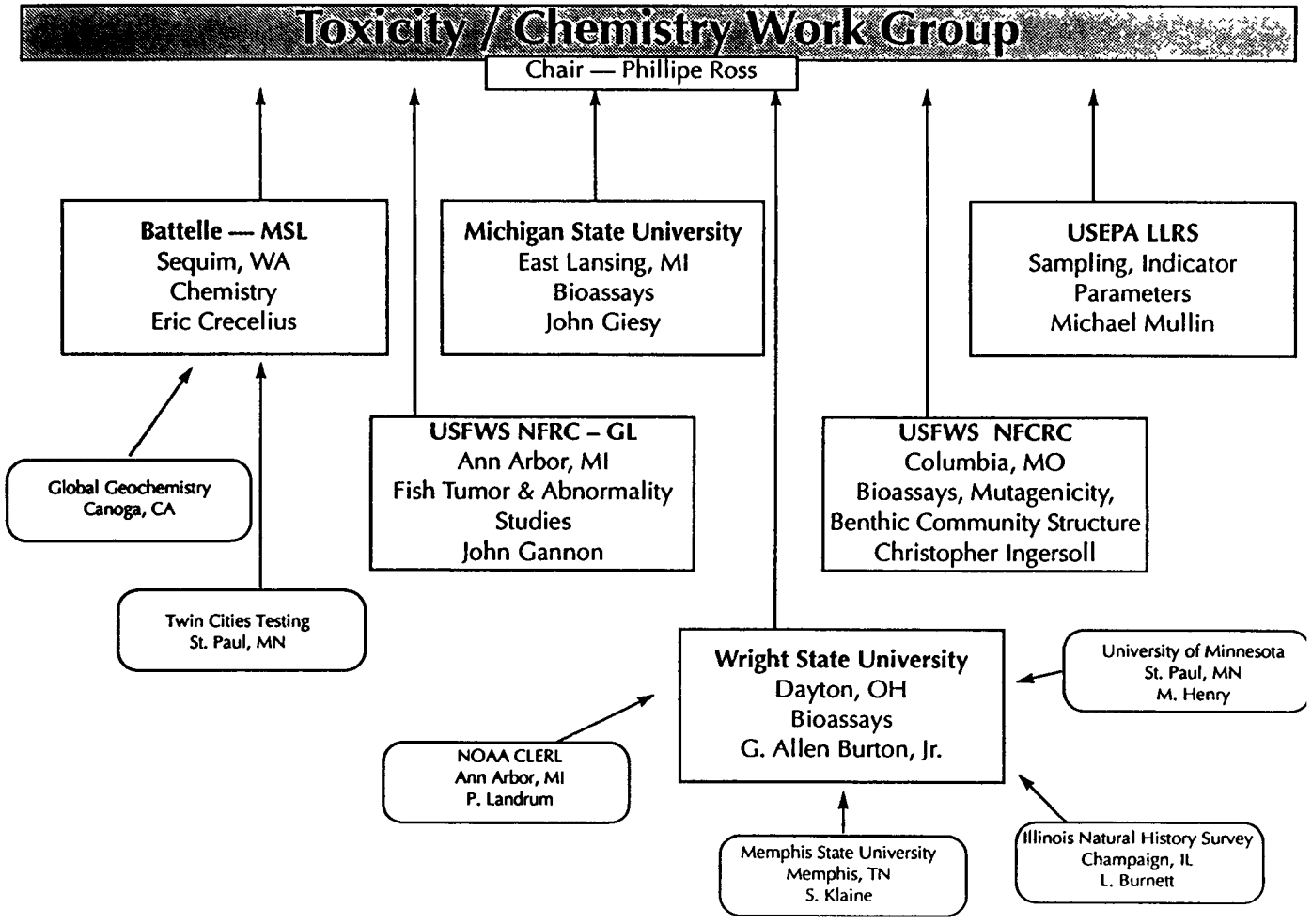

Figure 4. T/C Workgroup Organizational Chart.

There will be four kinds of sampling stations to be used for the ARCS program sediment testing:

- Reconnaissance stations,
- Master stations,
- Priority master stations, and
- Extended priority master stations.

Figure 5 shows the types of tests done at the various stations in each category. Sediment sampling and mapping are two of the primary responsibilities of the Large Lakes Research Station (LLRS) located in Grosse Ile, Michigan. A more complete description of the sampling activities of the LLRS is provided in Section 4.1.

Sediment surveys at each area of concern will be conducted in five phases. The five phases should be conducted in the following sequence:

1) pre-survey phase,
2) reconnaissance survey phase,
3) inter-survey phase,
4) supplemental survey phase, and
5) post-survey phase.

In the pre-survey phase, existing information on sediment contamination at each priority consideration area should be obtained and reviewed. Based on this information and discussions with various investigators who have worked in the area, a transect/station grid will be prepared to guide sampling and sediment profiling throughout the AOC. An initial set of ten master station surficial sediment samples will be collected using a Ponar grab sampler or box corer. Detailed analyses, including testing for both inorganic and organic contaminants will be performed on these samples. This data will then be correlated with the results of the reconnaissance stations where only a limited number of "indicator parameters" are run (described in following text).

During the reconnaissance survey phase, acoustical soundings will be made to map the physical distribution of sediments to aid in selecting sampling sites. Numerous sediment core samples (100 to 200 per area) will be collected at this time to be tested for a set of indicator parameters which can be run relatively quickly and inexpensively on a large number of samples. The core horizons will be visually characterized and photographed during the core collection process.

The core samples obtained during the reconnaissance survey will be analyzed during the inter-survey phase for the following indicator parameters at the LLRS laboratory:

- Ammonia (in sediment elutriates),
- Conductivity (in sediment pore waters)
- Metals (cadmium, chromium, copper, iron, lead, nickel, and zinc),
- Microtox™ (Photobacterium phosphoreum) bioluminescence assay (in sediment elutriates),

TYPES OF ANALYSES	TYPES OF SAMPLING STATIONS			
	Reconnaissance Stations	Master Stations	Priority Master Stations	Extended Priority Master Stations
INDICATOR PARAMETERS				
BENTHIC COMMUNITY				
DETAILED CHEMISTRY				
TIERED BIOASSYAS o Photobacterium o Selenastrum o Daphnia o Chironomus riparius o Hyalella o Pimephales				
AMES AND MUTATOX				
COMPARATIVE BIOASSAYS o Photobacterium o Selenatrun o Daphnia o Hyalella o Ceriodaphnia o Lemna o Pimephales o Hydrilla o Diaporeia o Hexagenia o Panagrellus o Bacterial enzymes				
BIOACCUMULATION				

Figure 5. T/C Workgroup Analytical Matrix by Station Type.

- Organohalogens (Br, Cl, and I),
- pH,
- Sediment grain size fractions,
- Solvent extractable residue,
- Total/volatile solids, and
- Total organic carbon.

In principle, the indicator parameters will correlate with other measurements of contamination and toxicity. Therefore, use of the indicator parameters will allow the detailed analyses from the few master stations to be extrapolated throughout the site, based on correlations between reconnaissance and master station data. Information from these analyses and from profiling data obtained during the reconnaissance survey will be used to prepare three-dimensional contamination maps during the post-survey phase. Maps of bottom topography and sediment layer thickness will also be prepared.

Based on the results of the bottom profiling and indicator parameters, an additional second set of ten master stations per AOC will be identified for sampling during the supplemental survey phase (resources permitting). Sediments from the second set of ten master stations will be collected, homogenized, and shipped to the same analytical laboratories for physical, chemical, and biological characterization as in the pre-survey phase.

Toxicity testing and a broader spectrum of toxicity testing (goals 2 and 3) will be performed using various bioassays in a tiered approach to make efficient use of analytical resources. The results of analyses at one tier are used to select which samples will undergo testing at the next tier. Fewer samples are analyzed in each successive tier since the tests become increasingly more time-consuming and costly. Tier I testing focuses on acute toxicity testing, benthic community structure and mutagenicity testing while Tier II focuses on partial life-cycle toxicity. Tier III testing focuses primarily on full life-cycle toxicity and bioaccumulation. The primary laboratories involved in the bioassay and toxicity testing are Michigan State University (MSU) in East Lansing, Michigan, the National Fisheries Contaminant Research Center (NFCRC) in Columbia, Missouri, and Wright State University (WSU) in Dayton, Ohio. Bioaccumulation studies will be performed at MSU and the National Fisheries Research Center-Great Lakes (NFRC-GL) in Ann Arbor, Michigan.

Tier I testing includes the use of the following methods on elutriates of the sediment samples obtained from all the initial ten master stations:

- Daphnia magna, 48-hr mortality test,
- Microtox™ (Photobacterium phosphoreum), 15-min luminescence test, and
- Selenastrum capricornutum, 24-hr carbon-14 uptake test.

Tier I testing also includes the use of chemical extracts obtained from sediment samples to assess any mutagenic activity using the Ames Salmonella microsome test as well as the determination of benthic community structure. In addition, selected invertebrates, fish, and amphibians may also be tested including midge (Chironomus tentans and Chironomus riparius), amphipods (Hyalella azteca),

cladocerans (Ceriodaphnia dubia), fathead minnows (Pimephales promelas), rainbow trout (Salmo gairdneri), or bluegill sunfish (Lepomis macrochirus).

Approximately one-half of the samples undergoing Tier I testing are selected for Tier II testing which consists of the Hyalella azteca, 7- and 14-day whole sediment growth, survival, and reproduction tests. Approximately one-quarter of the samples undergoing Tier I testing will also go through Tier III testing. Tier III testing consists of the following two tests:

- Hyalella azteca: 28-day whole sediment growth test, and
- Pimephales promelas: 10- and 28-day whole sediment bioaccumulation test.

Selection of samples for Tiers II and III are made to satisfy two conditions. Sediments with low acute toxicity form the majority of the selections, while some with moderately acute and highly acute toxicity are included to provide and appropriate range over which to evaluate the tiered testing system. Other bioassays may be added as deemed necessary by the T/C workgroup.

In order to provide guidelines for future contamination surveys, it is necessary to compare the results of the limited suite of bioassays to a larger set of bioassay methods. Therefore, a selected number of sediment samples will undergo a broader spectrum of bioassays. The additional bioassays, their various endpoints, and phases to be tested on the selected samples include:

- Microtox™ (Photobacterium phosphoreum), 15-min luminescence, elutriate,
- Selenastrum capricornutum: 48- and 96-hr growth, elutriate,
- Daphnia magna: 96-hr mortality, elutriate,
- Daphnia magna: 7-day reproduction, sediment,
- Chironomus tentans: 10-day mortality, sediment,
- Chironomus tentans: 10-day growth, sediment,
- Chironomus riparius, 14- and 28-day mortality, sediment,
- Chironomus riparius: 14-day growth, sediment,
- Hyalella azteca: 7- and 14-day mortality, sediment,
- Hyalella azteca: 14-, and 28-day reproduction, sediment,
- Ceriodaphnia dubia: 7-day mortality, sediment and elutriate,
- Ceriodaphnia dubia: 7-day reproduction, sediment and elutriate,
- Lemna minor: 4-day frond growth, sediment,
- Lemna minor: 4-day chlorophyll-a, sediment,
- Pimephales promelas: 7-day mortality, sediment,
- Pimephales promelas: 7-day growth, sediment,
- Pimephales promelas: 7-day terata, sediment,
- Hydrilla verticillata: 14-day root length growth, sediment,
- Hydrilla verticillata: 14-day shoot length growth, sediment,
- Hydrilla verticillata: 4-day chlorophyll-a, sediment,
- Hydrilla verticillata: 4- and 7-day dehydrogenase activity, sediment,
- Diporeia sp.: 20-day mortality, sediment,
- Diporeia sp.: 20-day avoidance, sediment,

- Diporeia sp.: 20-day uptake, sediment,
- Hexagenia limbata: 10-day mortality, sediment,
- Hexagenia limbata: 10- and 28-day growth (molting frequency), sediment,
- Hexagenia limbata: 10-day uptake, sediment,
- Panagrellus redivivus: 96-hr mortality, elutriate,
- Panagrellus redivivus: 96-hr growth (development), elutriate,
- Bacterial enzymes: 2-hr activity, sediment, and
- Artificial substrates: 28-day community indices, sediment.

The resulting information to be obtained from this effort will be compared with the results of the limited suite of bioassays. Several of these bioassays also yield dose-response information, which will be useful in the Risk Assessment/Modeling workgroup's assessment efforts. This broader spectrum testing on a limited number of samples also provides a check on the effectiveness of the tiered testing system.

Samples of sediments, sediment extracts (elutriates and pore waters), and fish tissue (from the bioaccumulation assays) collected in the ARCS program will be subjected to numerous chemical analyses to satisfy the fourth goal of the T/C workgroup. These analyses include a wide variety of inorganic and organic chemicals important to understanding sediment contamination problems in the AOCs. The bulk of the chemical analyses for the T/C workgroup will be performed by Battelle-Marine Science Laboratory (MSL) located in Sequim, Washington. The chemical parameters include:

- Total organic carbon (TOC) in the sediment,
- Free and acid volatile sulfides (AVS),
- Extractable metals,
- Metals (silver, arsenic, cadmium, chromium, copper, iron, mercury, manganese, nickel, lead, selenium, and zinc),
- Organo-metals (methylmercury and tributyltin),
- Polynuclear aromatic hydrocarbons (approximately 16 compounds),
- Polychlorinated biphenyls (total and approximately 20 congeners),
- Chlorinated pesticides,
- Chlorinated dioxin and furan congeners, and
- Semi-volatile chlorinated compounds.

A more complete list of the organic compounds to be analyzed is presented in section 4.2.

Fish tumor and abnormality identification on the brown bullhead (Ameiurus nebulosus) will also be performed as part of the T/C workgroup testing program (goal 5). The brown bullhead has been selected as the primary fish due to its intimate contact with the bottom sediments. The white sucker (Catostomus commersoni) or carp (Cyprinus carpio) will serve as secondary fishes. Surveys will be conducted in the Buffalo, Ashtabula, and Saginaw Rivers to determine the incidence of external abnormalities and internal tumors. A goal of eighty-five individual fish will be collected and targeted for field necropsy and histopathological examination at each area.

At a very limited number of master stations, the extended priority stations, a 10-day fathead minnow (Pimephales promelas) bioaccumulation assay will be conducted using bulk sediment samples. Upon completion of the assay, chemical analyses of the fish tissue will be conducted to determine the update of sediment contaminants into the organism. Chemical analyses will include all the tests described for satisfying the fourth goal of the T/C workgroup.

2.3.4 Risk Assessment/Modeling Workgroup

The Risk Assessment/Modeling workgroup (RA/M) is responsible for the evaluation of environmental and human health impacts resulting from contaminated sediments and the development of techniques for assessing the environmental impacts resulting from the implementation of remedial alternatives. An organizational chart displaying the laboratory name, laboratory location, the dominant type of analyses to be performed at the laboratory, and the principal investigator is presented in Figure 6. A mini-mass balance approach will be taken to provide the predictive capabilities necessary to determine such impact. The assessments will serve to identify and develop techniques and tools for performing sediment-related hazard evaluations. Assessments will consider the difficult task of separating the effects of sediments from those of the water column or other sources. A system for prioritizing sites with contaminated sediments will be developed and applied to the five priority consideration areas to provide a comparative framework for assessing multiple sites in need of remediation.

The primary objectives of the RA/M workgroup are:

1) hazard evaluation, and
2) prioritization system development.

Both of these objectives will be discussed with the tasks needed to accomplish the objectives in the following text.

The phrase "hazard evaluation" refers to the overall evaluation of impacts to all receptors of concern resulting from exposure to sediment contaminants and consists of several discrete assessments (objective 1). The ultimate purpose of the hazard evaluation is to determine the existing and future health risks and effects (e.g., carcinogenic, reproductive, or systemic effects, community structure impacts, etc.) presented to human and environmental receptors (aquatic, avian, mammalian) from direct or indirect contact with sediment contaminants under different remedial options. The hazard evaluation is comprised of four assessments, namely, exposure, human health risk, aquatic hazard, and wildlife hazard assessments. The exposure assessment is an integral part of the human health risk assessment and the aquatic and wildlife hazard assessments, and is not usually separated out as such. However, since the activities involved in performing the exposure assessment are different than those involved in performing a risk or hazard assessment, the separation has been made in this document.

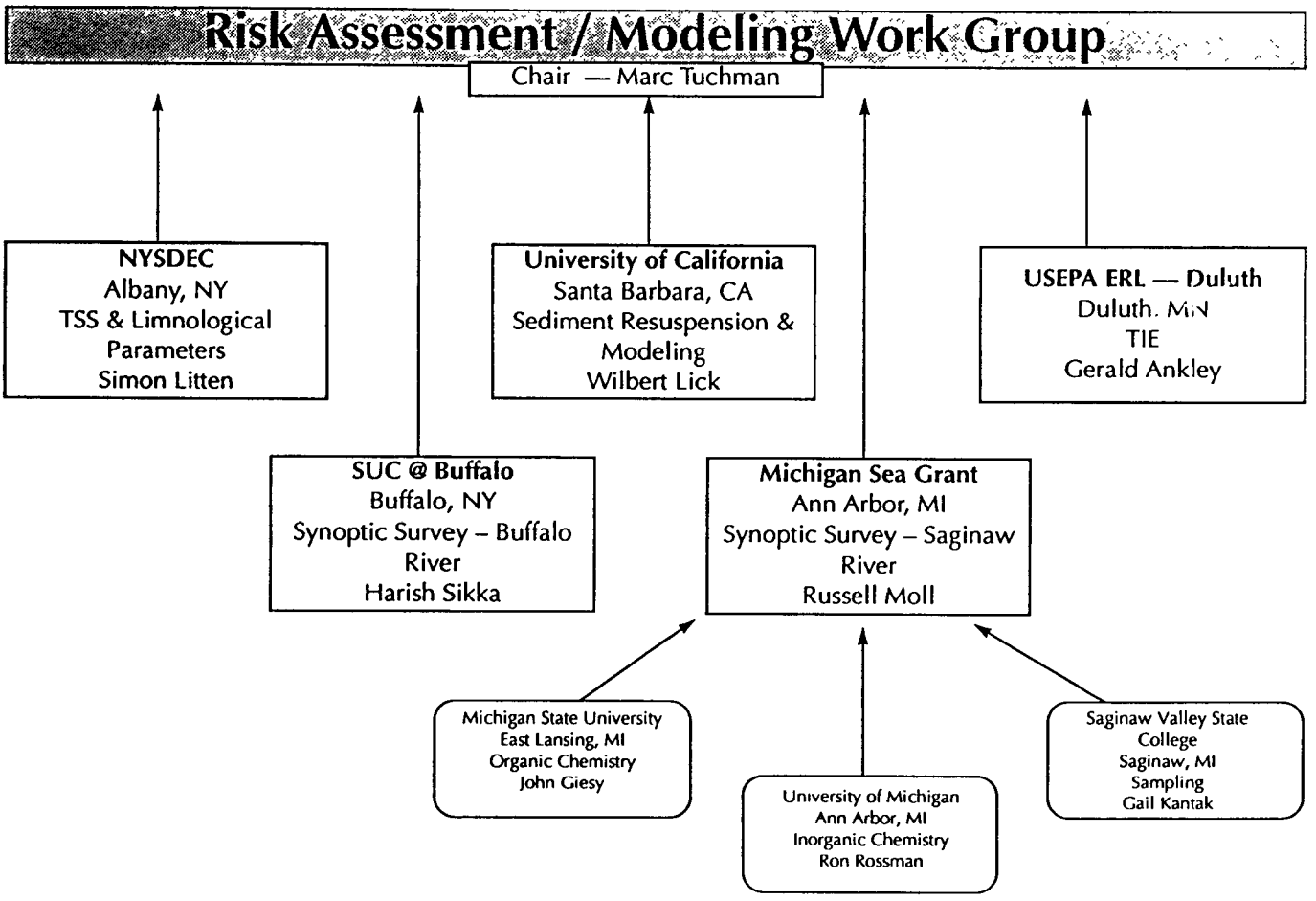

Figure 6. Risk Assessment/Modeling Workgroup Organizational Chart.

Two levels of evaluation are proposed in this program plan, namely, baseline and comprehensive hazard evaluations. Baseline human health hazard evaluations will be performed for all five priority demonstration areas and will be developed from available site-specific information. The baseline hazard evaluations will describe the hazards to receptors under present site conditions or the "no action" alternative. This baseline assessment will examine all potential pathways by which humans may incur risk from exposure to sediments at a given location.

Comprehensive hazard evaluations will be performed for the Buffalo River and Saginaw Bay areas. These evaluations will describe the hazards to receptors under different remedial alternatives. A variety of remediation scenarios will be examined as part of the comprehensive evaluation. These will include examining selective removal or capping of "hot spots", source control, or dredging of an entire river, among others. Additionally, the comprehensive risk assessment will examine risk from losses of selected remedial alternatives. The following remedial alternatives may be considered in this phase of the comprehensive evaluation:

- Capping,
- Immobilization/stabilization,
- Extraction,
- Chemical treatment,
- Biological treatment, and
- Confined disposal.

These remedial alternatives will be considered by the Engineering/Technology (E/T) workgroup, which will determine the input of contaminants, after remediation, presented by each alternative. The RA/M workgroup will use these contaminant loading estimates to estimate exposure and hazards to receptors and compare them to the "no action" alternative.

As a component of both the human health risk assessment and the aquatic and wildlife hazard assessments, the exposure assessment strives to describe or predict the receptor's exposure to sediment-related contaminants. The assessment of direct or indirect exposure to sediment contaminants by receptors of concern will vary with the type of receptor considered (human, aquatic, avian, or mammalian), the exposure route (ingestion, inhalation, and/or dermal uptake) and the exposure parameters (exposure magnitude, duration, and frequency).

Probable human exposure routes which may need to be addressed in this assessment include: (1) intake of sediment contaminants through the consumption of aquatic and avian wildlife into which sediment contaminants have bioaccumulated, (2) intake of sediment contaminants through ingestion of sediments (particularly in children between the ages of two and eight), and (3) dermal uptake of sediment contaminants resulting from recreational use of nearshore contaminated areas. Other exposure routes, such as inhalation of volatile contaminants in sediments or ingestion or inhalation of contaminants from drinking water supplies tainted by sediment contaminants may also be important on a site-specific basis.

Exposure assessments for aquatic biota will be evaluated in part by work being performed for the T/C workgroup. A suite of bioassays on the toxicological effects of sediment contaminants are planned by the T/C workgroup, including those to provide dose-response information. These data, along with existing information, will be the basis for the aquatic biota hazard assessment.

Exposure assessments for piscivorous avian and mammalian wildlife will focus mainly on the uptake of sediment contaminants through the consumption of biota into which sediment contaminants have bioaccumulated. Other routes of exposure may also be of importance such as intake of contaminated suspended particles in whole water or direct uptake of sediment contaminants dermally. The feasibility of analyzing these routes will be considered.

The input needed to perform the exposure assessments will be provided by existing information, information obtained from the T/C workgroup, though the RA/M workgroup's modeling efforts, and through the performance of selected field exposure studies.

The purpose of exposure modeling is to provide a predictive tool to evaluate future exposures (and consequently hazards) if present conditions are maintained ("no action") or if cleanup actions are undertaken. The development and validation of models will proceed in two phases (Figure 7). Phase I will focus on developing modeling tools using existing information.

Phase II will validate the approaches developed in Phase I by obtaining current synoptic information about the area via five or six sampling days on a given river system. Data will be collected on flows, contaminant loadings, and concentrations in the water column of both the particulate and dissolved phases. This work will be conducted on the Buffalo and Saginaw Rivers. The State University College at Buffalo (SUC-B) in Buffalo, New York will conduct the sample collection on the Buffalo River while a team of Universities in Michigan (a consortium of the University of Michigan in Ann Arbor, Michigan, Michigan State University located in East Lansing, Michigan, and Saginaw Valley State University in University Center, Michigan) will conduct the sampling program on the Saginaw River. To support the food chain model (to be discussed), fish species will also be collected and analyzed. For the Buffalo River, the food chain model will concentrate on carp, while for the Saginaw River, the walleye (Stizostedion vitreum) fishery and other forage fishes will be sampled and analyzed. These data will then be used to calibrate the exposure models. Without calibration, there would be little confidence in the exposure models results.

The contaminants to be selected for modeling purposes will be chosen based on fish advisories, concerns cited in the respective remedial action plans, and results obtained from Toxicity Identification Evaluation (TIE) of the sediments as part of the ARCS program. TIE involves the manipulation of the extracted pore waters from the sediments followed by toxicity testing. The manipulations of the pore water are intended to change the toxicity of the sample and subsequent toxicity tests using either Pimephales promelas or Ceriodaphnia dubia as test organisms. Based on the manipulations, inferences can then be drawn about the physical-chemical characteristics of the toxicants. The TIE work will be performed by the Environmental Research Laboratory in Duluth, Minnesota (ERL-D) and WSU.

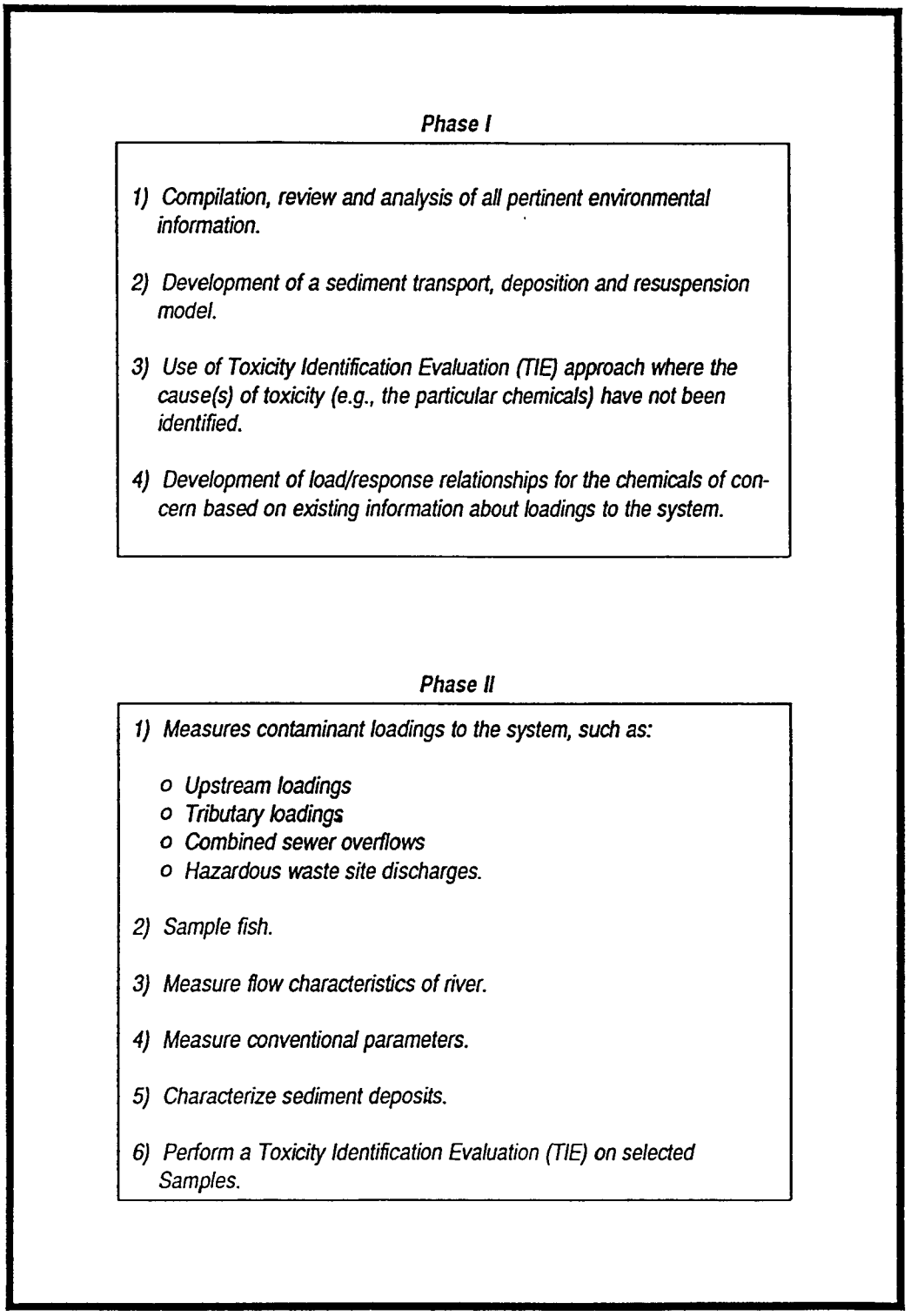

Figure 7. Components of Phase I and II Exposure Modeling Efforts.

The parameters that will be examined in the Buffalo River priority consideration area by SUC-B include the following contaminants:

- Total polychlorinated biphenyls (PCBs),
- DDT,
- Dieldrin,
- Chlordane,
- Benzo(a)pyrene,
- Benzo(a)anthracene,
- Benzo(b)fluoranthene,
- Benzo(k)fluoranthene,
- Chrysene,
- Pb, and
- Cu.

The contaminants to be analyzed and modeled for the Saginaw River AOC will be:

- Total PCBs,
- Pb,
- Cu, and
- Zn.

The primary objectives of the mass balance modeling studies include the demonstrations of available mass balance techniques and how they may be used as an aid in addressing management questions concerning the remediation of contaminated sediments. The mass balance studies will be designed to allow estimates of the effects of remedial alternatives, using information provided from other ARCS programs, in order to estimate the response of the AOCs to these alternative remedial actions in terms of toxicity and concentrations of contaminants in the water, sediment, and biota. In the mass balance approach, the law of conservation of mass is applied in the evaluation of the sources, transport, and fate of contaminants. The approach requires that the quantities of contaminants entering the system, less quantities stored, transformed, or degraded in the system, must equal the quantities leaving the system. Once a mass balance budget has been established for each pollutant of concern, the approach can be used to provide quantitative estimates of the effects of changes in that budget.

A mass balance model is the means by which the mass balance approach is applied to a natural system. The application of the mass balance method involves the quantification of the sources, transport, and fate of contaminants. The specific components of the exposure modeling study are described below.

1) Hydrodynamic Model Application: The complex interaction of flows in the Great Lakes (due to upstream inflows and changes in lake elevation) requires that a hydrodynamic model be applied in order to estimate flows. For the systems of concern in the ARCS modeling studies, the model will be multi-dimensional in order to provide resolution of lateral as well

as possible vertical gradients in addition to longitudinal gradients in transport characteristics.

2) Sediment Transport Model: A model of cohesive sediment transport will be applied in order to predict the interactions between transport, deposition, and resuspension processed under various meteorological and hydrological conditions. This model will provide predictions for use in the transport of sorbed contaminants and resuspension of toxic sediments. The model will aid in assessing the "no-action" alternative by providing estimates of burial rates and the effects of dredging on the system by providing estimates of sediment transport and times required to refill dredged areas. The application of a sediment transport model is of particular importance in these studies due to the lack of historical sediment data.

3) Contaminant Exposure Model: Time variable exposure models will be applied in order to predict the effects of water and sediment transport, as well as the effects of sorption and kinetic processes such as volatilization and degradation, on the concentrations of certain critical contaminants. Modeling studies will be conducted concurrently of the riverine portions of the systems and affected bays or lakes. The contaminant exposure model will assess the effects of loading and various remedial alternatives on the system. The models will be applied to estimate load/response/uncertainty relationships, which will aid in addressing the study objectives. The models will also provide information that will be used by the food chain model to estimate the contaminant body burdens in fish species due to varying exposure concentrations in water and sediment.

4) Toxicity Model: Since it may not be possible to relate exposure concentrations to toxic effects, it will be necessary to construct a toxic unit model of the system in order to estimate the probability of toxicity in response to various meteorological and hydrological conditions to evaluate the impacts of proposed remedial alternatives. The toxic unit model will utilize information from the hydrodynamic and sediment transport models as well as data from sediment transport models to estimate the probability of toxic events.

5) Food Chain Model: A model of the food chain will be utilized to estimate the response of varying exposure concentrations on contaminated concentrations in the biota. The model will use data collected as part of the study in order to construct a simple food chain model as well as evaluate certain hypothetical food chains (due to reintroduction of some species) using information obtained from the other studies.

The study will utilize existing models and methods. The model which will be used as a framework for the study is the Water Quality Analysis Program - WASP4 (Ambrose et al., 1988). This model will be used to integrate predictions from other models (e.g., hydrodynamic and sediment transport) in order to estimate contaminant concentrations in the water, sediment, and biota. The WASP4 model provides a consistent modeling framework for eutrophication, toxics transformation and transport, bioaccumulation, and food chain effects. It is maintained and distributed by the

Center for Exposure Assessment Modeling in Athens, Georgia and has been widely distributed throughout the world.

Field sampling programs will be designed to provide information required for the application of mass balance models. Synoptic surveys are planned for six sampling days for the lower Buffalo and Saginaw Rivers by SUC-B and MSG, respectively. Data will be collected on two low flow days, representative of low flow steady-state conditions. Samples will also be collected during a high flow event lasting 3 to 4 days. The sampling stations will be selected to allow estimates of pollutant influxes to and effluxes from the AOCs. Samples will be integrated over the width of the river system and possibly over depth. Where significant stratification is encountered, samples will be taken at discrete depths at several locations. The data collected during the synoptic surveys will include flows, loading and concentration data for solids and chemicals in both water and suspended solids. Studies of selected conventional parameters will be collected at a greater frequency in order to aid in the calibration of the hydrodynamic and sediment transport model and in order to aid in estimating yearly loadings. Data on sediment contamination will be collected as part of the studies of other ARCS workgroups. The types of data to be obtained are briefly described below.

1) Hydrodynamic Data: Data for the calibration of the hydrodynamic model will include historical data as well as data collected as part of the field studies. Historical data are available on flows, water surface elevations at the mouth of the Buffalo and Saginaw Rivers, meteorological data, and concentrations of some conventional constituents such as temperature, conductivity, etc. These data will be obtained concurrently with field studies. In addition, water surface elevation data, velocity and discharge measurements, and wind velocity and direction data will be obtained.

2) Sediment Transport Data: Data for the calibration of the sediment transport model will rely on historical data, such as U.S. Army Corps of Engineers dredging records. Data on sediment characteristics (e.g., grain size, water content, etc.) will be collected during the sediment surveys. Further, suspended solids will be collected concurrently with the river sampling and suspended solids data will be collected either during high flow events on the Buffalo River or hourly during certain periods on the Saginaw River in order to support the sediment transport model. Finally, "shaker" studies will be conducted to estimate the resuspension characteristics of the bottom sediments in the Buffalo River by the University of California at Santa Barbara (UCSB) located in Santa Barbara, California.

3) Contaminant Exposure Data: Historical ambient water, sediment, loading, and food chain data will be used for the calibration of the exposure model, whenever possible. In addition, surveys will be conducted to identify spatial variability in the system during certain low flow periods. Further studies will be conducted to identify pollutant loadings and ambient pollutant concentrations in water, sediments, and biota.

   a. Pollutant Loadings: Pollutant loading will be estimated and/or measured from point and non-point sources. Historical data will be assessed to estimate loadings from point sources as well as measurements acquired concurrently with the ambient water quality

studies. Loadings from combined sewer overflows (CSOs) will be estimated based on a limited field sampling program (24 samples at 10 CSOs) and storm water modeling in the Buffalo River study. CSOs were not identified as a significant pollutant loading source in the Saginaw River and will therefore not be sampled. Loadings for contaminants and suspended solids from upstream tributaries will be based on six daily averaged measurements. Historical contaminant, suspended solids, and flow data, as well as data from the suspended solid survey, will be used to extrapolate these measurements to annual loading rates. An analysis of the uncertainty of these estimates will also be performed.

b. Ambient Water Concentration: Ambient data for particulate and dissolved contaminants as well as conventional parameters will be obtained over the six scheduled sampling days.

c. Sediment Data: Data for sediment concentrations will be collected as part of separate sampling studies planned for the RA/M workgroup.

4) Food Chain Data: Data will be collected for carp in the Buffalo River and their stomach contents analyzed in order to establish a relationship between carp contaminant concentrations and their benthic forage. Carp were selected for analysis for two reasons. First, there are presently advisories in effect for consumption of carp in the Buffalo River. Second, the available resources limit the possibility of collection data to support an evaluation of fish species with a more complex food chain. Data will be collected for a minimum fifteen carp (divided into three age classes) for analysis. Sampling in the Saginaw River will concentrate on walleye and its food chain due to the importance of the walleye fishery in the area.

The final phase of this approach will be to verify and calibrate the models in Phase I using the site-specific data collected during Phase II.

The activities involved in the preparation of the individual risk and hazard assessments vary depending upon the area evaluated, the receptors, and the endpoints considered. It is primarily a paper exercise combining information on exposure to and toxicity of sediment contaminants. The baseline assessments will use existing data while the comprehensive assessments will use the results obtained from the exposure modeling work to predict future risk.

Cancer risks and non-cancer hazards potentially incurred resulting from direct and indirect exposure to sediment contaminants will be considered. Risks and hazards will be calculated using methods recommended by the USEPA risk assessment guidelines of 1986 and other generally recognized risk assessment procedures. Uncertainties in the risk assessment will be stated, as will the assumptions, and discussion on the overall meaning of the risk assessment will be developed. Toxicological information required to calculate risks or hazards may not be available for all chemicals found in the demonstration areas. Therefore, the baseline risk assessment will identify information which is required for the evaluation but not available, and such needs will be recommended to the

AIC for resolution. As part of the comprehensive evaluations planned for the Buffalo River and Saginaw Bay, target sediment concentrations (i.e., chemical concentrations below that associated with unacceptable risks and hazards) will be calculated for chemicals identified as responsible for the majority of the risk or hazard.

One of the more potentially important impacts of some chlorinated organic compounds, such as PCBs, are their potential adverse developmental effects upon infants and children. Recent epidemiological evidence exists that suggests developmental effects have occurred in young children whose mothers were heavy consumers of Great Lakes fish. Given the relationship between sediment and fish contamination, this toxicological endpoint should be assessed in the ARCS program. However, this endpoint is not easily assessed in a quantitative fashion using the existing risk assessment methodology commonly employed by the USEPA. This arises from the hypothesis that the contaminants, to which the infant or child is exposed through placental transfer and breast-feeding, is the result of the mother's body burden of the chemical. This maternal body burden is the result of her lifetime of contaminant intake, not only that occurring during pregnancy. Assessment would require complex pharmacokinetic modeling, an approach which is not well developed in the environmental assessment field.

Given the difficulties which exist in quantifying this hazard, it is beyond the scope of the ARCS program to address this issue in any great depth. However, ARCS would be remiss if it did not address the issue at all. Therefore, the RA/M workgroup will pursue the option to develop the existing epidemiological information, discuss the relationship between sediments, fish consumption, human body burden, and human-to-human chemical transfer, and discuss the inadequacies of present assessment techniques to describe the problem.

A numerically-based ranking system which synthesizes assessment variables and produces objective priorities will be designed to allow remedial priorities to be set for each of the Great Lakes AOCs (objective 2). Development of numerically-based ranking systems will provide a method for integrating hazard and risk assessments within and between individual AOCs. The result will be a prioritization procedure that can be used in a comprehensive strategy for the management of contaminated sediments by Federal, State, and Provincial governments to guide the development of RAPs and Lakewide Management Plans.

During the ARCS program, a database for each of the five priority consideration areas will be obtained and will contain assessment variables which range from site-specific factors (e.g., measurements and/or predictions of heavy metal and organic contaminants, acute and chronic toxicity, mutagenicity, bioaccumulation potential, benthic species composition, and resuspension potential) to broad scale factors (e.g., fish tumor incidence rates, fish and waterfowl consumption advisories, loading to receiving waters, beach closings, drinking water hazards, human risk from fish consumption, and socioeconomic considerations). These factors will be integrated for use in a decision-making framework to determine which site(s) should be targeted for remedial action. As much as possible, this assessment will be based on a minimum data set common to all five priority consideration areas obtained by the three technical workgroups.

For the decision-making process, assessment factors will be synthesized to evaluate the sites with regard to remediation. For remedial evaluation, a ranking system will be used which (1) is numerically-based, (2) accommodates a multi-disciplinary database (chemical concentrations, ecotoxicity, model predictions, human risk, cost, etc.), (3) synthesizes and reduces the database to an understandable context, (4) produces objective output, (5) illustrate quantifiable differences between sites, and (6) established remedial priorities. The priorities established by the ranking system will then be viewed in terms of remedial goals, the likelihood of successful remediation, cost-benefit, and the technologies available to achieve these goals.

The following tasks anticipated for this activity provide site ranking and integration of information about individual sites or AOCs:

1) investigate methods of ranking and decision support analysis to determine what other approaches should be incorporated for the ARCS program,
2) develop a ranking method to integrate measures of hazard, risk, and cost,
3) develop a method of ranking sites which can be applied to the Great Lakes region, by State and Provincial jurisdictions, or smaller sub-regions (i.e., individual lake watersheds), and
4) calibrate and test the ranking procedure and integration procedure on the five priority consideration areas being investigated during the ARCS program.

This work will be closely coordinated with the data collection and assessment activities of the T/C workgroup. Data collection and toxicology studies will be specifically designed to provide information for the integration and ranking system selected.

2.3.5 Engineering/Technology Workgroup

The primary responsibilities of the Engineering/Technology workgroup will be to evaluate and test available removal and remedial technologies for contaminated sediments, to select promising new technologies for further testing, to demonstrate alternatives at priority consideration areas, and to estimate contaminant losses during remediation. An organizational chart displaying the laboratory name, laboratory location, the dominant type of analyses to be performed at the laboratory, and the principal investigator is presented in Figure 8. The E/T workgroup will seek technologies that are available, implementable, and economically feasible. Both removal and *in situ* alternatives will be considered.

To fulfill these responsibilities, the following tasks will be required:

1) review of technical literature,
2) evaluation of applicability of technologies for bench-scale studies,
3) develop recommendations for pilot-scale demonstration,
4) estimate contaminant losses during remediation,
5) collect sediments for bench-scale testing,

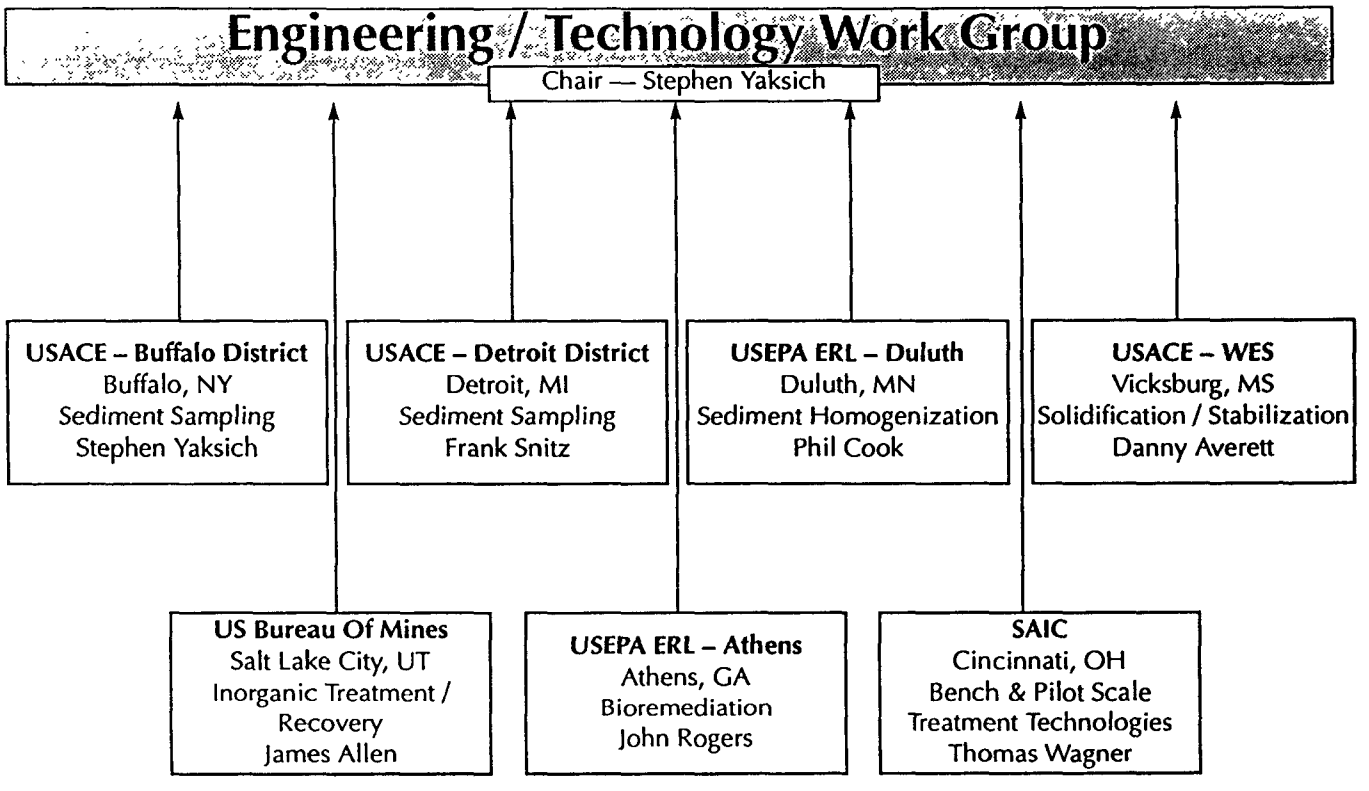

Figure 8. Engineering/Technology Workgroup Organizational Chart.

6) store and analyze sediments,
7) bench-scale testing of selected treatment technologies,
8) treatment technologies for inorganic contaminants,
9) workshop on bioremediation technologies,
10) evaluation of solidification/stabilization technologies,
11) conduct pilot-scale demonstrations, and
12) development of options for priority consideration areas.

Each of these tasks will be discussed individually in the following text.Existing literature on contaminated sediment treatment technologies will be reviewed for the ARCS program focusing on the updating of present knowledge on the selection and use of technologies for removal and transport of contaminated sediments, placement/disposal of material at disposal sites, treatment technologies, as well as *in situ* techniques (task 1). Previous technology assessments and field demonstration studies conducted by the USEPA, USACE, and other laboratories will be reviewed for applicability.

The applicability of treatment technologies to priority consideration areas will be evaluated based upon the nature and degree of contamination at the site (task 2). Treatment technologies identified in Task 1 will be matched with the contaminants present at a given site, the level of contamination, and volume of sediments to which technology can be applied to remediate the sediments. Each technology will be evaluated based on cost, effectiveness, volume of material to be handled, level of existing contamination and levels of cleanup required.

The E/T workgroup will develop recommendations for the selection of sites and technologies for pilot-scale demonstrations (task 3). The selection of technologies which are available for pilot-scale demonstration may be limiting since there will probably not be enough time to scale-up developmental techniques which require elaborate physical or mechanical plants. All proprietary vendors that already have portable pilot-scale plants available for demonstration will be considered. A few technologies can be demonstrated using commercially available equipment.

Another limiting factor that must be considered during the recommendation development process is the availability of sites for the demonstrations. Site availability may be the major determinant as to which technologies can be demonstrated during the ARCS program. Most pilot-scale demonstration are performed at the site of contamination. The site of a demonstration must be secure so that accidents, spills, or emissions can be controlled. The use of existing, operational confined disposal facilities (CDFs) will be selected as the most viable sites for demonstrations since the land acquisition and site preparation processes for demonstrations is a very time-consuming process and requires resources beyond the scope of the ARCS program. Other options, such as close collaboration with Superfund projects and/or the Superfund SITE program, will be explored.

Contaminant inputs that may occur to the environment during and after implementation of the remedial alternative will be assessed (task 4). Models available to calculate losses during dredging, volatilization losses, leaching losses, runoff and effluent concentrations will be reviewed. Models will be selected to calculate the annual losses to the environment resulting from each treatment

technology evaluated. These contaminant loads to the environment will be supplied to the RA/M workgroup who will assess the human and environmental health impacts associated with each of the remedial alternatives. These tasks will be accomplished the USACE Waterways Experiment Station (WES) located in Vicksburg, Mississippi and the USEPA Environmental Research Laboratory in Athens, Georgia (ERL-A).

The bench-scale tests (to be discussed) require sediments for testing from the five priority consideration areas (task 5). The "same" sediment samples will be used to evaluate and compare similar demonstration projects. Therefore, it is necessary to collect, characterize, and preserve large-volume sediment samples from each of the areas. Sediment samples will consist of homogenized, moist composites of samples from a contaminated region within the priority consideration area. Sediments will be collected for all five areas for bench-scale studies. Additional samples will be collected for the pilot demonstration projects.

The sediment samples will be homogenized and split into representative subsamples in a wet condition during the operations of task 6. The wet subsamples will be provided in a variety of convenient sizes for use by the various investigators. The procedure to accomplish this task will be the same that has been previously applied to sediments from Lake Ontario and the Fox River/Green Bay (Great Lakes National Program Office, 1989), and has been validated for organic carbon and organochlorine contaminant homogeneity. Wet samples will be stored in a cold room at 4° C.

The basic characterization of the sediment will be performed by ERL-D and will include the following parameters:

- Total organic carbon,
- Total inorganic carbon,
- Particle-size distribution,
- Density of the dry material,
- Total sulfur content,
- Acid volatile sulfides,
- Oil and grease,
- Total PCBs,
- Polynuclear aromatic hydrocarbons (PAHs),
- Metals, and
- Hg.

Particularly promising technologies identified in Task 3 will be evaluated in bench-scale tests using sediment from the priority consideration areas (task 7). As used here, bench-scale tests are defined as tests that are done on a few grams to kilograms of sediment. The selection of which technology to use on which priority consideration area will depend upon matching the characteristics of each technology to the contamination present at the given area. A brief description of the technologies available for remediation of contaminated sediments will be provided in later text in this section.

Bench-scale testing will provide preliminary feasibility data and design data for pilot-scale demonstrations of selected technologies. As used here, pilot-scale tests are those that involve up to several cubic meters of sediments. Several laboratories/companies have been identified to perform various portions of the bench-scale testing program and will thus receive contaminated sediment samples for the priority consideration areas dependant upon the expected results of their remedial process.

Science Applications International Corporation (SAIC) of Cincinnati, Ohio, under the direction of the Risk Reduction Engineering Laboratory (RREL) in Cincinnati, Ohio, will be contracted to test the B.E.S.T™ extraction process, two different varieties of low temperature thermal stripping (LTS), wet air oxidation, and incineration remedial processes. Sediments from the Sheboygan River, Ashtabula River, and Grand Calumet Harbor will be tested by the USEPA's RREL-Cincinnati laboratory using the Base Catalyzed Destruction (BCD) process for removal of PCBs. Sheboygan River sediments will also be sent to ECO-Logic in Ann Arbor, Michigan, for testing with their hazardous waste destructor. Sediments from the Buffalo, Saginaw, Grand Calumet, and Ashtabula priority consideration areas will be sent to Chemical Waste Management, Inc. located in Riverdale, Illinois, for their solvent extraction procedure.

The treatment technologies for the remediation of inorganic contaminants (task 8) will be the primary responsibility of the Bureau of Mines (BOM) - Salt Lake City research facility in Salt Lake City, Utah. The BOM will examine the treatment options that include the extraction and recovery of metals from the contaminated sediments. These techniques include physical separation processes using gravity, magnetic properties, and flotation processes. Treatment options will be evaluated using sediment samples from three of the priority consideration areas with metal contamination problems, namely, Buffalo River, Grand Calumet River, and Saginaw Bay.

A workshop on bioremediation processes (task 9) will be conducted by ERL-A in which presentations will be made describing site characterizations of the five ARCS priority AOCs located in the United States and for Hamilton Harbor, Ontario. Once the overviews of these areas have been presented, the remainder of the workshop will be devoted to discussing related laboratory and field studies and the applicability of biological remediation processes of sediment-based contaminants, in particular, for the degradation of organic compounds. The workshop will be conducted to arrive at a consensus on the direction bioremediation testing should take for the ARCS program, due to the relative diversity of approaches being attempted in this field, and the high potential of this form of remedial action.

Besides removal and disposal, chemical solidification/stabilization (CSS) techniques are probably the most proven techniques for remediation of contaminated sediments. CSS techniques will be investigated for the Buffalo River sediments to accomplish task 10. The scope of the study will involve laboratory preparation of CSS samples using Buffalo River sediment and one of the following binders/additives: portland cement, lime/fly ash, kiln dust, and portland cement with powdered activated carbon. A range of binder-to-sediment ratios will be screened and an optimal ratio will be selected for detailed evaluation. Effectiveness will be measured by comparing leaching

results, unconfined compressive strength, and durability under wet/dry and freeze/thaw cycles at WES.

Pilot-scale demonstrations will be scheduled to start in FY 1991 and continue through FY 1992 (task 11). The scale of the pilot demonstrations will be several hundred cubic yards of sediment. Full-scale demonstrations would address in the range of 5000 to 10000 cubic yards of sediment. Pilot-scale demonstrations will only show the unit process (e.g., extraction). They will not include the full treatment train (e.g., dredging, storage, sorting, dewatering, extraction, destruction of extract, solidification, and final disposal) that a full-scale demonstration would. Pilot-scale demonstrations could be performed either on-site or at an off-site location.

Based upon the information gained in the earlier tasks, concept plans for sediment remedial options (task 12) will be developed for each priority consideration area. The costs of applying the selected options will be calculated. In addition, estimates will be made on the losses of contaminant that might result from applying the remedial actions. The RA/M workgroup will use this and other information to evaluate the hazards associated with each remedial option. These plans will also serve to identify data gaps that need to be filled in order to complete the process of selecting the best remedial options for each priority consideration area. The concept plans to be developed will present three different remediation scenarios for each priority consideration areas. These plans will provide useful information to the State and local groups responsible for the development of sediment RAPs.

A brief description of each of the remedial technologies that are under consideration or are part of the ARCS program and presented in Table 1 follows:

- Solidification/stabilization: The addition of binding materials to produce a more stable solid material that is more resistant to the leaching of contaminants. Typical binding materials used include portland cement, fly ash, kiln dust, blast furnace slag, and proprietary additives.

- Inorganic treatment/recovery: The physical or chemical separation of sediments into different fractions that may be more or less contaminated. Since sediment contaminants usually associate themselves with fine-grained particles like silts and clays, their separation from the bulk sediment could significantly reduce the volume of material requiring advanced treatment.

- Bioremediation: The use of microorganisms such as bacteria to reduce the toxicity of sediment contaminants by degrading them through biological action. Bioremediation has been used in the treatment of waste waters and contaminated soils.

- Base catalyzed destruction (BCD) process: This chemical process, formerly call KPEG nucleophilic substitution, reduces the toxicity of chlorinated hydrocarbons (such as PCBs) by removing chlorine atoms and replacing them with alkali metals such as potassium.

Table 1. Treatment Technologies to be Demonstrated at the Priority Consideration Areas.

TECHNOLOGIES	PRIORITY CONSIDERATION AREAS and Scale of Demonstration				
	ASHTABULA RIVER	BUFFALO RIVER	GRAND CALUMET RIVER	SAGINAW BAY	SHEBOYGAN HARBOR
Solidification/ Stabilization		Bench[c]	Bench[e]		
Inorganic Treatment/ Recovery		Bench[b]	Bench[b]	Bench[b]	
Bioremediation					Bench[d] Pilot[d]
KPEG Nucleophilic Substitution	Bench[a]		Bench[a]		Bench[a]
B.E.S.T. Extraction Process		Bench[a]	Bench[a,e]	Bench[a]	
CF Systems Solvent Extraction			Bench[a]	Bench[a]	
Incineration			Bench[a]		
Low Temperature Thermal Stripping		Bench[a]			
Wet Air Oxidation		Bench[a]	Bench[e]		
Eco-Logic Destruction Process					Bench[f]
In-Situ Stabilization					Bench[d] Pilot[d]
Acetone Extraction (Rem-Tech)					Bench[d]
Aqueous Surfactant Extraction					Bench[d]
Taciuk Thermal Extraction					Bench[d]
Sediment Dewatering Methods					Bench[d]

Legend: a = performed for ARCS Program by contractor
b = performed for ARCS Program by Bureau of Mines
c = performed for ARCS Program by Army Corps of Engineers/Waterways Experiment Station (WES)
d = performed by Superfund Potentially Responsible Parties
e = performed for U.S. Army Corps of Engineers by Indiana University - N.W. or Corps' WES
f = performed for Canada

- Basic extraction sludge technology (B.E.S.T.) extraction process: This extraction separates contaminated sediments into three fractions: a solid fraction that contains the inorganic contaminants (such as heavy metals); and oil fraction that contains the organic contaminants (such as PCBs); and a water fraction that may contain residual amounts of the original sediment contaminants. Alone, B.E.S.T. does not destroy any contaminants but may significantly reduce the volume of material requiring advanced treatment.

- Critical fluids (CF) systems solvent extraction: This extraction performs the same functions as the B.E.S.T. process, but instead of the solvent used by B.E.S.T., the CF System's process utilizes gases at critical temperature and pressures (propane and carbon dioxide), which reduces the cross-contamination of the end products with the solvent. The propane is simply exposed to normal pressure and temperature where it returns to its gaseous state.

- Incineration: Incineration involves the high temperature destruction of organic contaminants in a furnace. It has been used for the disposal of municipal and hazardous wastes.

- Low temperature thermal stripping: LTS removes volatile organic contaminants by heating the sediments to temperatures lower than those used in the destructive incineration process. This process is not intended to permanently destroy contaminants but may result in a sediment that is more easily disposable.

- Wet air oxidation: Organic contaminants are destroyed by exposing them to elevated temperature and pressures. This process was developed over 30 years ago and has been successfully used to treat municipal sewage sludge.

- Low energy extraction: This extraction separates contaminated sediments into the same fractions as described for the B.E.S.T. process. It uses a combination of solvents to remove PCBs and other organic contaminants from the sediment.

- ECO-Logic destruction process: A thermochemical process that uses high temperature and hydrogen gas to destroy organic contaminants.

- *In Situ* stabilization: This process involves the covering or armoring of sediment deposits with geotextiles, plastic liners, or graded stone. It thus prevents the disturbance and resuspension of contaminated sediments which could lead to a release of sediment contaminants back into the water column.

- Acetone extraction (Rem-Tech): Acetone is used as a solvent to extract PCBs from contaminated sediments.

- Aqueous surfactant extraction: This process is similar to the low energy extraction process previously described. Instead of applying acetone, however, this process uses

aqueous surfactant to remove PCBs. Ultrasonics may be employed to improve extraction efficiencies.

- Taciuk thermal extraction: A thermal separation process similar to low temperature thermal stripping. The sediments are heated in a oxygen-free atmosphere which aids in the removal of organic contaminants.

- Sediments dewatering methods: These techniques to remove water from contaminated sediments include air drying, consolidation, and filter processes. They may be necessary prior to the application of a treatment technology that works inefficiently in the presence of water.

2.3.6 Communication/Liaison Workgroup

The role of the quality assurance program in the Communication/Liaison (C/L) workgroup is nonexistent since this workgroup generates no measurement data. However, since the C/L workgroup is an integral part of the ARCS program, a brief overview of their activities is presented here.

The Communication/Liaison Workgroup is responsible for the dissemination of up-to-date information regarding the ARCS program and related activities to elected officials, government agencies, and the interested public. This workgroup will also provide feedback from those interested parties to the technical workgroups and other ARCS committees.

These responsibilities will be accomplished by the completion of the following tasks:

1) continual workgroup interaction,
2) preparation and dissemination of general and site-specific information materials on the ARCS program and on contaminated sediments in general,
3) mailing list compilation and maintenance,
4) solicitation of public input through news updates, press releases, questionnaires, public meetings, and informal dialogue,
5) development and maintenance of library repositories for contaminated sediment and ARCS program materials in the five priority areas,
6) on-site coordination of public meetings and press briefings,
7) slide show preparation and dissemination,
8) video preparation and dissemination, and
9) guidelines for public participation and community outreach plans, when appropriate.

The C/L workgroup will prepare press releases, fact sheets, and other such materials for dissemination to interested Federal and State agencies, elected officials, and the public at regular intervals. Quarterly ARCS updates will be produced and published. They will provide information not only on the ARCS program activities, but also on cooperative efforts and information sharing

with other projects (such as USEPA's Superfund program, Environment Canada's contaminated sediment research, etc.) and on more general topics, such as current scientific research that relates contaminated sediments to ecological impacts on the Great Lakes. Updates on activities specific to the priority consideration areas will be included in the fact sheets or produced and disseminated separately, as needed. Press releases will be coordinated and issued by the C/L workgroup member representing USEPA's Office of Public Affairs.

Representatives from the C/L workgroup will travel to the priority consideration sites to inform the public and media about the ARCS program, ongoing field work, research activities and results. Public meetings will be held at all five of the ARCS program site locations. Based on the experience gained in dealings at the five priority consideration areas, the C/L workgroup will produce guidelines for public involvement for future contaminated sediment demonstration projects.

A slide show will be developed to aid in the discussion of contaminated sediments. The narrative developed in conjunction with the slide show will discuss current contaminated sediment problems, pollutants, ARCS objectives, and remedial options.

Section 3

Sampling Strategy

3.1 Selection of Areas of Concern

Forty-two areas of concern have been identified by the International Joint Commission (a binational organization composed of commissioners from Canada and the United States) in the Great Lakes Basin Ecosystem (Figure 2). These AOCs are sites where general or specific objectives of the Great Lakes Water Quality Agreement are not met and such failure has caused or is likely to cause impairment of beneficial use or of the area's ability to support aquatic life. Impairment of beneficial use means a change in the chemical, physical, or biological integrity of the Great Lakes ecosystem sufficient enough to cause any of the following: restrictions on fish and wildlife consumption; tainting of fish and wildlife flavor; degradation of fish and wildlife populations; fish tumors or other deformities; bird or animal deformities or reproductive problems; degradation of benthos; restriction on dredging activities; eutrophication or undesirable algae; restrictions on drinking water consumption, or taste and odor problems; beach closings; degradation of aesthetics; added costs to agriculture or industry; degradation of phytoplankton or zooplankton populations; or loss of fish and wildlife habitat.

From the original list of forty-two AOCs selected by the IJC, five AOCs were named in the authorizing legislation for testing in the ARCS program The five selected ARCS AOCs (Figure 1) are:

- Sheboygan Harbor,
- Grand Calumet River/Indiana Harbor,
- Saginaw River/Bay,
- Ashtabula River, and
- Buffalo River.

Of the five selected AOCs, two are currently undergoing testing/remediation through the Superfund program, namely, Sheboygan Harbor and Ashtabula River. Since there is a considerable amount of Superfund work in ongoing and due to limitations of funding, these two sites will undergo minimal testing in the ARCS program. Therefore, the ARCS program will concentrate its resources and efforts on the remaining three AOCs.

3.2 Toxicity/Chemistry Workgroup Sampling Strategy

The T/C workgroup will analyze four different levels/types of samples in order to satisfy the original goals of its part of the ARCS program. These levels are the master station, priority master station, extended priority master station, and reconnaissance station. Some of the different sample types require unique samples to be obtained while other samples are differentiated by the amount

of testing that will be performed on the sediment. A more detailed description of the different sample types and their site selection is provided in the following text.

3.2.1 Selection of Master Stations

In general, the selection of master station locations will be determined by the members of the T/C workgroup. Three primary considerations that will be used during the selection process will be:

1) the availability of historical sediment contaminant concentration data and contaminant maps from each AOC,
2) input from local authorities, including discussions of present and future public uses as well as present and historic contaminant discharges or sources, and
3) a desire to provide some degree of complete geographic coverage of the entire AOC.

Stations will usually be positioned along the sides of the dredged shipping channel since these shallow areas are usually the location of sediment deposition zones. Areas of soft sediment will preferably be selected due to sampling considerations. When possible, samples will be collected in each AOC that represent a gradient of contaminant concentrations ranging from stations considered to be relatively uncontaminated to known "hot spots" of high pollutant content as identified from work performed for the first two considerations.

3.2.2 Selection of Priority Master Stations

Approximately one-half of the master stations will be selected to be designated as priority master stations. These stations will be selected to represent sediments with a wide range in the degree of contamination present in each AOC. The priority master station sediments would thus include samples with little to no appreciable quantities of contaminants as well as from "hot spot" where notably high contaminant concentration levels have been identified. These sediments will undergo the same testing that is performed for the master stations with an additional suite of comparative bioassays (Figure 5). The additional suite of bioassays will be used to assist in the selection of optimal sediment toxicity test assays (i.e., which organisms are most sensitive to the presence of given contaminants or suites of contaminants), to provide comparisons with the IJC recommended test battery, and to aid determinations of biologically significant contaminant levels in "grey" areas where contaminant levels are likely to produce some acute and chronic toxicity effects.

3.2.3 Selection of Extended Priority Master Stations

Most, if not all, of the sediments selected as priority master stations will undergo a bioaccumulation assay using Pimephales promelas. Upon completion of the assay, the actual sediment used in the bioaccumulation assay will undergo chemical analysis. If the potential exists for the bioaccumulation of a contaminant or suite of contaminants identified in the sediment, the priority master station will be designated as an extended priority master station and the fish tissue

will then undergo analysis for the suspected bioaccumulated contaminants. The extended priority master station sediments will most likely be an area of high contaminant levels (i.e., the "hot spot") in each AOC.

3.2.4 Selection of Reconnaissance Stations

In general, the locations of the indicator stations will be chosen to give a more complete coverage of the AOC than could be provided by the sampling of the master stations. Selection of the reconnaissance stations will be based on historical data plus the interpretation of the results from sub-bottom profiling (a more detailed description of the sub-bottom profiling may be found in section 4.1.1.3). The profiling tracings will be examined for indications of soft sediment, sediment layering, physical discontinuities, and other features of interest which can be used to separate distinct depositional episodes and, thus, possibly different contamination levels.

The profiling and coring scheme for the AOCs will be designed to accomplish two goals, namely, (1) to conduct a "zone reconnaissance" of sediment quality throughout the whole study area and (2) to perform a more detailed "site mapping" of a known "hot spot" depositional area. Chronologically, the sub-bottom profiling of the area will be conducted first, accompanied by the more or less simultaneous interpretation of the profiling tracings. After review of the tracings, sediment cores will be collected using a Vibra-corer system (to be discussed in more detail in section 4.1.1.2). Approximately 60 cores will be collected from each AOC.

For the "zone reconnaissance" sampling, samples will be collected throughout the AOC from positions generally across the river channel from each other with an occasional core being collected from the center of the navigation channel. The zone reconnaissance will also involve collecting cores at the initial master stations so that correlations can be made between the detailed analyses performed on the master stations and the indicator parameter analyses that will be performed on the reconnaissance stations. The correlated data will then be used to produce three-dimensional mapping of contamination and toxicity from each AOC.

The site mapping will involve the intensive collection of cores throughout the area of the "hot spot". Approximately 30 cores (one-half of the cores to be collected per AOC) will collected on a grid system that covers the entire "hot spot". The potential sites will be about 25 m apart along seven transects between the navigation channel and one bank of the river. The intensive sampling of the "hot spot" will provide detailed information on the contaminant levels and distribution should the area be selected for a limited remediation demonstration.

3.3 Risk Assessment/Modeling Workgroup Sampling Strategy

Sampling for the RA/M workgroup will consist predominantly of the collection of samples to support the mini-mass balance/synoptic surveys on the Buffalo and Saginaw Rivers. These efforts will include the collection of the water column samples, simultaneous measurements of river discharge and associated water quality parameters, and sampling of fish populations. For the

Buffalo River system, the sampling of combined sewer outfall (CSO) discharges will also be undertaken. CSOs were not identified as a contaminant source for the Saginaw River and therefore will not be sampled. Two additional river characterization studies will be conducted on the Buffalo River AOC by the RA/M workgroup. The rationales for the various RA/M workgroup surveys and studies will be discussed separately in the following text.

3.3.1 Mini-Mass Balance/Synoptic Surveys

The basic goal in the sampling design for the mini-mass balance/synoptic surveys is to collect information about the river system during several periods of low flow (or quasi-steady state) conditions as well as during at least one high flow event (after a major storm system has passed through the AOC or during the spring snow melt). These data will provide information on the relative importance and amplitude of point and non-point pollutant sources to the AOC on both a temporal and a spatial scale. These same data will also serve as a primary information source for the mass-balance, near-field dispersion, far-field dispersion, and food chain models to be used by the RA/M workgroup. Samples will be collected from fixed stations (six in the Saginaw River AOC and 7 within the Buffalo River AOC) for all sampling events to measure pollutant influxes to the AOC, ambient concentrations within the AOC, and effluxes to the lake, harbor, or bay.

Under low flow conditions, numerous measurements will be taken throughout the AOC to determine dissolved contaminant concentrations in the water column and on the suspended sediment. Additional measurements of the river flow conditions (i.e., flow velocity and direction, sediment load, thermal stratification, etc.) and water quality parameters (such as pH, conductivity, temperature, dissolved oxygen, chlorophyll-a content, etc.) will be made simultaneously with the collection of the water column samples.

Samples collected during the high flow event will undergo the same basic measurements as the samples collected under low flow condition and will be collected at the same station locations. Data derived from these samples will be used to give an indication of the variation in pollutant concentration with discharge.

Combined sewer outfalls will be sampled to quantify the input of contaminants from the storm waters that drain the City of Buffalo. CSOs have been identified as a potential source of inorganic and organic contaminants in the Buffalo River RAP (NYSDEC, 1989). Ten CSOs will be selected and sampled to give a coverage of the Buffalo River AOC. The criteria used in the selection of these sites include:

1) the ability to obtain samples from a manhole up-pipe of the outfall,
2) runoff inputs from major land use categories present in the AOC,
3) good spatial resolution within the AOC,
4) outfalls representing a large contributing area and have a pipe diameter of greater than 61 cm, and
5) the past use of the given outfall in the model to be applied to the AOC.

Selected CSOs will be collected during one storm overflow event. Samples will be taken during at least two additional CSO events at a selected outfall to provide a preliminary assessment of pollutant level variability from different storm events.

Fish samples will be collected at both the Buffalo and Saginaw River AOCs. Fish will be collected throughout the entire stretch of the river that has been designated as the AOC. Carp will be collected as the primary fish in the Buffalo River while walleye will be sampled in the Saginaw River. Carp were chosen to be sampled in the Buffalo River due to their abundance and representativeness of the river's bottom feeders. Walleye was selected in the Saginaw River AOC due to its abundance, the importance of the walleye fishery at the AOC, and past use of the walleye in bioaccumulation studies thereby allowing for comparison of results and modeling efforts through time. Fish samples will be collected and analyzed to determine the bioaccumulation of the contaminants in the food chain of the AOC. A minimum of 45 from each AOC will be collected and separated into three representative age classes to allow for the determination of bioaccumulation rates and variability through the life-cycle of the selected species. These data will then be correlated to the quantities of contaminants in the water column and suspended sediments to determine biotic uptake rates and bioaccumulation potentials.

3.3.2 Sediment Transport Studies

The sediment transport studies involve the determination of the resuspension potential of the bottom sediments. The sampling strategy involves collecting samples and testing resuspension potential throughout the entire AOC. Actual sampling sites will be selected after discussion with the members of the field crew from LLRS that has sampled both master and reconnaissance stations on the Buffalo River and has done preliminary mapping of the Buffalo River. The primary consideration will be to perform tests at sites with muddy bottom sediments since these sediments are most easily resuspended by natural high flow events. Sites will be divided into two classes, namely, deep (greater than 10 feet deep) and shallow (less than 10 feet deep) waters, if muddy bottom sediments can be identified in each class.

3.3.3 Hydrodynamic Studies

This study involves the collection of total suspended solids data and other limnological parameters, such as water temperature, conductivity, and velocity, during high flow events in the river. These data will be used in the calibration of hydrodynamic and sediment transport models to be employed by the RA/M workgroup modelers. The primary goal of this exercise will be to obtain data from the upper and lower boundaries of the Buffalo River during an event large enough to initiate bottom scour of the river bed. Samples will be collected from bridges over the Buffalo River and Cazenovia Creek (the major tributary to the Buffalo River in the AOC) at the upper reaches of the AOC and from a bridge near the mouth of the river.

3.4 Engineering/Technology Workgroup Sampling Strategy

The E/T workgroup's sampling strategy consists of simply gathering enough sediments from one or two locations within an AOC to supply all the bench scale remediation processes with the same initial sediment after it has been homogenized. Therefore, all remedial activities will be starting from the same baseline contaminant concentrations to allow for the determination and comparison among the effectivenesses of the remedial processes in the removal of a given class or classes of contaminants (i.e., PCBs, PAHs, and/or metals). The sediments to be collected will be grossly contaminated with a given class or classes of contaminants. The collected samples should contain several representative contamination scenarios that have been identified in the Great Lakes basin so that the results can then be applied to the remediation of not only the AOC but other sites as well. Site selection will be based on historical data, the results of the sediment characterization from the T/C workgroup efforts, and discussions among members of the three technical workgroups.

Section 4

Field and Laboratory Operations

This section outlines the operational and logistical operations required for the sampling, sample preparation, and analyses of the sediments for the ARCS program. Specific information on the step-by-step action will be presented in the QAPjPs prepared by the participants in the ARCS program. This section is divided into two parts, namely, field and laboratory operations. Further subdivisions will be made by workgroup since the sampling and laboratory activities and goals are different for each of the three technical workgroups.

4.1 Field Operations

Field operations will be undertaken for all three technical workgroups. Written SOPs will be provided for all sampling activities and will be included in the QAPjP submitted in conjunction with the sampling effort. The goals of sample collection for the T/C workgroup will include the collection of sediments from all the master stations to be used for sediment characterization (including both chemical and physical properties of the sediment) and toxicity testing. The T/C workgroup will also be responsible for the collection of the reconnaissance station sediment samples that will be used in the quantification of indicator parameters. Further, maps of the bottom sediments will be generated from the field data obtained using seismic and resistivity mapping techniques by the T/C workgroup. The field operations for the RA/M workgroup will include sampling for the synoptic surveys (mini-mass balance surveys) on the Buffalo and Saginaw Rivers, sediment resuspension potential determinations, and total suspended solids measurements (including miscellaneous flow and water quality parameters) to be used in the modeling efforts of the RA/M workgroup. The E/T workgroup's field operations will include the collection of bulk sediments to be used and distributed to various laboratories during the testing of the selected remedial technologies. Discussion of the personnel involved in the field operations, sample preparation/homogenization techniques, sample storage and custody procedures, and a brief overview of the methods to be used in obtaining samples for the ARCS program will be presented in the following text. The rationale for the selection of the sampling locations has already been presented in Section 3 of this document.

4.1.1 Toxicity/Chemistry Workgroup Field Operations

The Large Lakes Research Station at Grosse Ile, Michigan will be responsible for the collection of all the sediments for the T/C workgroup. This sampling includes the collection of all the master and reconnaissance stations as well as mapping the contaminated sediments. The project officer of the LLRS effort is Dr. Michael D. Mullin of the USEPA. Field operations will be under the direction of John C. Filkins of the USEPA and Joseph Rathbun of AScI Corporation. AScI Corporation is a primary subcontractor to the USEPA at the LLRS research field station. More detailed information on the sampling efforts of the T/C workgroup will be presented in the LLRS QAPjP.

4.1.1.1 Master Stations

The general locations of the master stations will be determined by the T/C workgroup prior to the field crew actually going to the AOC. The exact locations of the sampling sites will be determined in the field by the sampling crew which will have two considerations in the site selection process. The two considerations will be (1) the presence of soft sediments and (2) the ease of relocating the station at a later date should it become necessary. For logistical reasons, it is occasionally necessary to move a station from its intended location to a more practical position.

At each master station, the sampling process will consist of four steps. These steps are as follows:

1) site location,
2) benthos sample collection,
3) bulk sediment collection, and
4) sample preparation, labeling, and storage.

The first step will be to obtain the exact location of the collection site. Location information will be obtained after the sampling vessel has been securely anchored by a minimum of a three-way anchoring system. Site coordinates will be obtained using the Loran C navigation or the global positioning system. In addition, triangulation observations will be made at each station using local landmarks. Both sets of coordinates will be recorded in a bound logbook along with the date, time, weather conditions, and any pertinent comments.

The second step in the field sampling program will be to obtain the samples to be used to determine the benthic community structure. Five individual Ponar grab samples will be collected and sieved through a 500 μm sieve. Prior to the taking of the replicate grab samples, the sampler will be moved to avoid collection from the same spot. All material remaining on the sieve will be placed in an uniquely labeled (on both the outside of the jar as well as on paper inside the jar) canning jar and preserved with a 10% buffered formalin solution. Prior to shipping these samples to NFCRC-Columbia for determination and quantification of the benthos, the jars will be filled approximately two-thirds full or to cover the material with formalin, whichever is greater.

Collection of the bulk sediment sample (step 3) will be performed using either a Van Veen or Ponar grab samplers. Approximately 15 liters of sediment at master stations and approximately 120 liters of sediment at priority master stations will be required. Multiple grabs will therefore be required. To avoid the sampling of the same spot and to assure the collection of true surficial sediments, the sampler and sampling vessel will be moved slightly during the sampling process. Movement of the vessel will consist of changing the position along two or three of the anchor lines which will allow the vessel to shift its position slightly downstream. The sediment from the grabs will be transferred to 5-gallon plastic-bag lined buckets. Upon completion of sampling at a given site, all sampling equipment will be thoroughly rinsed with river water to remove any residual sediments.

Upon completion of the sampling effort, the sediments will be transported to the shore to be homogenized. Homogenization will consist of mixing the sediments in a cement mixer for 15 minutes. Homogeneity will be checked visually in the field. If the sediments appear to be heterogeneous after the first 15 minutes, an additional 15 minutes mixing in the cement mixer will be used. The mouth of the cement mixer will be covered with plastic sheeting to help limit the loss and exposure of the sampling crew to any volatile organic compounds present in the sediment. Once the sediment is determined to be homogeneous, the sample will be transferred to labeled, high-density polyethylene bottles. A 2-inch headspace will be left in each bottle to allow for later sample homogenization at the analytical laboratories. The bottles will be place in ice chests and surrounded with ice packs. Ice packs will be replaced as needed to maintain the samples in a chilled condition as near to 4° C as possible. Upon completion of sampling at a given site, all sampling equipment will be thoroughly rinsed with clean tap water to remove any residual sediments. Just prior to shipping, fresh ice packs will be placed inside the ice chests along with a shipping manifest indicating sample numbers, sample volumes, and collection dates. Samples will be shipped by next-day delivery to the LLRS laboratory for storage. Samples will be maintained at the LLRS laboratory in walk-in coolers at 4 ± 2° C in the dark.

A unique sample identification coding scheme, developed at LLRS, will be used to clearly label and identify the numerous sediment samples that are part of the program. The coding scheme consists of a unique 11-digit sample number. The number can be used to identify the collection site, survey number, transect number, station number, sample type, replicate, and sample fraction (Figure 9). This number will be assigned to each sediment, fish, or benthos sample and will be recorded in the field log and on the sample container. This number is the only number that will be used and will be accepted for the reporting of the final data in the ARCS program.

4.1.1.2 Reconnaissance Stations

The location of the reconnaissance stations will be determined in the field and selected to achieve two primary goals, namely, to obtain as complete as possible coverage of the entire AOC and to obtain a zone of intensive sampling around a known "hot spot". Indicator station locations will be chosen based on historical data plus the interpretation of the results from the sub-bottom profiling (to be discussed). A more complete discussion of the rationale and sampling design used for the selection of reconnaissance stations was presented in section 3.2.4.

The sampling process at each reconnaissance stations will consist of two primary steps. The steps are (1) site location and (2) sediment core collection. The first step will be to obtain the exact location of the collection site. Location information will be obtained after the sampling vessel has been securely anchored by a minimum of a three-way anchoring system. Site coordinates will be obtained using the Loran C navigation or the global positioning system. In addition, triangulation observations will be made at each station using local landmarks. Both sets of coordinates will be recorded in a bound logbook along with the date, time, weather conditions, and any pertinent comments.

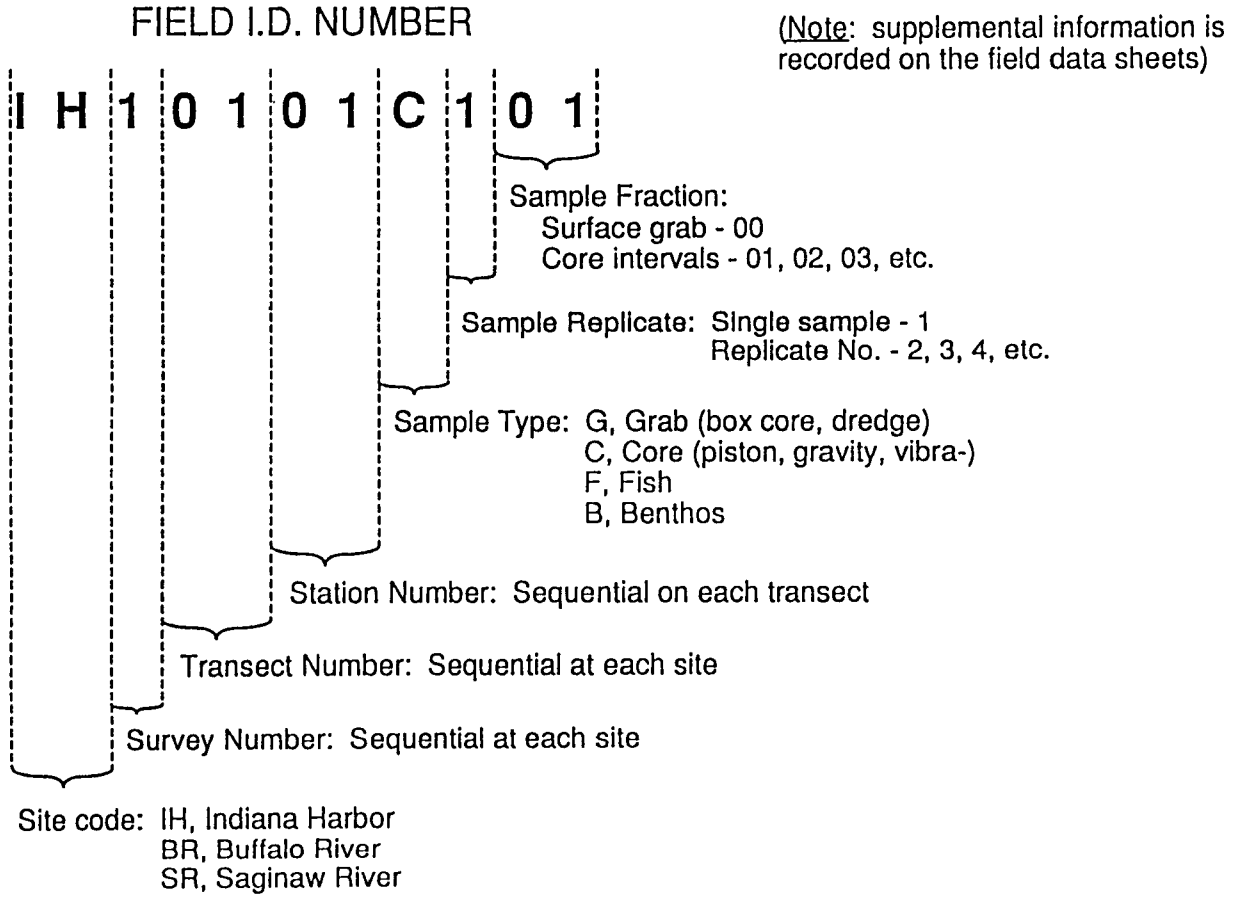

Figure 9. ARCS Sample Identification Coding System.

The second step in the field sampling program will be to obtain the core samples to be used to determine the indicator parameters. Once the sampling vessel is firmly anchored, core samples will be obtained using a Vibra-core unit. The core tube will be lined with a plastic core sleeve and secured at one end. The core tube will be securely attached to the vibrating motor head and lowered into the water. The vibrator unit will be activated upon contact with the sediments and the core will be pushed into the sediment until it is "refused". Upon retrieval of the core tube, the core sleeve will be removed and placed on a work table. The core sleeve will be cut and the core sliced in half lengthwise. Observations of sediment color, texture, smell, and layering will be made and recorded in the field logbook. Video tapes of each core will also be made while the core is laid out on the work table. The field crew will then slice the core laterally into approximately 2-foot sections which will be kept as individual samples. These samples will be placed in 4-liter polyethylene bottles and kept on ice until transported back to LLRS for laboratory analysis. Upon completion of sampling

at a given site, all sampling equipment will be thoroughly rinsed with river water to remove any residual sediments. Homogenization for the reconnaissance station samples will consist of mixing the sediments until visually homogeneous (i.e., uniform color, texture, and water content) at the LLRS laboratory. Samples will be maintained at the LLRS in walk-in coolers at 4 ± 2° C in the dark.

The same unique sample identification coding scheme, as discussed for the master stations, will be used to clearly label and identify the numerous sediment samples that are part of the ARCS program. This number will be assigned to each sediment sample and will be recorded in the field logbook and on the sample container. This number is the only number that will be used and will be accepted for the reporting of the final data in the ARCS program.

4.1.1.3 Sediment Mapping

The objectives of the sediment mapping program are to spatially map the extent and thickness of post-glacial bottom sediments in selected AOCs and to determine the degree of hardness of the surficial sediments. The mapping effort will be a part of the LLRS project under the direction of Dr. Michael D. Mullin with assistance from Dr. Robert W. Taylor of the University of Wisconsin, Milwaukee, Wisconsin. Ideally, the sediment mapping will be performed prior to the collection of the reconnaissance stations to help identify areas with soft bottom sediment deposits for potential core sampling. However, due to time constraints on the sampling surveys, the mapping of the sediments prior to sampling may not be possible and will thus be performed nearly simultaneously with sample collection of the reconnaissance stations.

Sediment mapping will be conducted using seismic and resistivity profiling equipment. The seismic profiling for the T/C workgroup will be performed using a Datasonics Model SBT-220 sub-bottom transceiver and a model TTV-120 towed transducer vehicle with transducer array. Resistivity data will be obtained using a current transmitter with a 1.5 kilowatt output at an 8 second period. Electrical resistivity potentials from a 20 electrode Schulumberger array will be collected and used to determine sediment clay content.

In portions of the AOC which are less than 100 meters wide, three equally spaced lines parallel to shore line will be surveyed. In wider stretches of the river, harbor, or bay, an additional series of diagonal lines forming a diamond pattern will overlay the parallel lines. Resistivity profiles may only be feasible along the parallel tracks due to instrument/system limitations. Time permitting, additional longitudinal tracks will be planned down the channel and along both sides of the river.

The seismic data will be used to map the thickness and extent of the bottom sediments. The resistivity unit will measure the electrical resistivity of the pore water in the sediment which can be directly related to the physical characteristics of the sediment, such as clay content, and be used as a auxiliary procedure for the seismic system. The profiling equipment will be connected to the Loran C navigation or global positioning systems which will periodically record the geographic position of the unit on the strip chart and computer record. The strip chart records of the distribution of the soft and consolidated sediments and water depth will be used to create a map

of soft sediment deposition areas and a three-dimensional distribution map of the sediment layers. When necessary, core samples will be collected to aid in the interpretation of the profiling results.

4.1.1.4 Fish Collection for Tumor and Abnormality Studies

Brown bullheads (Ameiurus nebulosus) will be collected from the Indiana Harbor/Grand Calumet River system by electroshocking. This method allows capture of live fish necessary for pathological examination yet is non-destructive to non-target species. Depending upon the depth of water, some supplementary sampling with gill nets, trawls, and/or trap nets may be necessary. The NFRC-GL, under the direction of Dr. John E. Gannon, will be responsible for the collection of the fish samples. If the brown bullheads are not found or are in insufficient number, the white sucker (Catostomus commersoni) will become the target species of bottom dwelling fish. The target number of fish to be collected is 85 with a minimum of 50 fish being considered adequate for the estimation of tumor frequency, although at a reduced confidence level.

4.1.2 Risk Assessment/Modeling Workgroup Field Operations

The State University College at Buffalo (SUC-B) in Buffalo, New York will be responsible for the collection of all the samples for the synoptic or mini-mass balance surveys to be conducted on the Buffalo River. This effort will include the collection of the Buffalo River water column, simultaneous measurement of river discharge and field-collected limnological parameters, and sampling of fish populations. SUC-B will also be responsible for the sampling of combined sewer outfall (CSO) discharges into the Buffalo River. The project officer of the SUC-B effort will be Dr. Harish C. Sikka of the Division of Environmental Toxicity and Chemistry. More detailed information on this portion of the sampling efforts of the RA/M workgroup will be presented in the SUC-B QAPjP.

The members of the Saginaw River team, a cooperative agreement among the University of Michigan, Michigan State University, and the Saginaw Valley State University, will be responsible for the collection of all the samples for the synoptic survey to be conducted on the Saginaw River. This effort will include the collection of the Saginaw River water column, simultaneous measurements of river discharge and field-collected limnological parameters such as water temperature, flow rates, pH, conductivity, etc., as well as the sampling of fish populations. The project officer of the MSG effort will be Dr. Russell A. Moll of the Center for Great Lakes and Aquatic Sciences at the University of Michigan in Ann Arbor, Michigan.

4.1.2.1 Mini-Mass Balance/Synoptic Survey Sampling

For the synoptic surveys, the field-collected limnological parameter list includes conductivity, water temperature, pressure (depth), dissolved oxygen, pH, percent light transmission, fluorescence (chlorophyll-a), and total incident radiation to the water surface. Field-collected parameters will be determined during each day of sampling at the sampling stations. More frequent measurements may be necessary to better characterize the river water and flow conditions in the synoptic survey AOCs. In the Buffalo River, the field-collected limnological parameters will be measured using the

Sea-Bird® Model SBE-25 Sealogger automated measurement system. In the Saginaw River and Bay, the Sea-Bird Electronics SEACAT SBE-16® recorder fitted with a Sea Tech Transmissometer will be used to measure conductivity, temperature, and light transmission. The HydroLab Surveyor II® field unit will be used in conjunction with the SEACAT recorder to collect data for water temperature, conductivity, pH, and dissolved oxygen in the Saginaw River. Total incident radiation will be measured using a LI-COR® system for both surveys. In addition to the field-collected limnological parameters, meteorological conditions will also be noted and recorded daily during sampling events.

Current velocity, direction, and water surface elevation will be made to determine river discharge at both AOCs. Current velocity and direction will be determined as a function of depth using a March-McBirney Model 301 Flow Velocity Meter in the Buffalo River while both Price and Weathermeasure current meters will be used in the Saginaw River. Water surface elevations will be read from staff gauges installed along the river banks or bridges by the USACE. A map of the bottom profile will be made using either a depth finder or be obtained from the USACE. This data used in combination with the measured currents will provide the discharge of the river at each station.

Prior to the sampling of the water column in the Buffalo River, determinations will be made as to whether the river is stratified or not. The direction of current flow will be the primary parameter used to determine if stratification of the river exists. The river will be considered stratified if the vertical velocity profile indicates reverse flow and the temperature profile (to be used as a confirmatory analysis) shows the presence of a thermocline. If the river is not stratified, water samples will be composited horizontally (width-integrated) along a transect at mid-depth. If the river is stratified, one horizontally composited water sample will be taken above the thermocline and another horizontally composited sample will be taken below the thermocline. Both samples will be maintained as unique and separate samples for analysis. Water column samples in the Saginaw River will only be composited horizontally (width-integrated) at mid-depth since stratification is not a concern at this AOC.

Water column samples for metals analysis will be collected using a Sigma streamline pump sampler, or equivalent. These samplers are designed to limit sample contamination and the intake rates have been approved by the USEPA. Prior to sampling at each transect, the intake line of the sampler will be rinsed at least three times or purged for 10 minutes with river water to help eliminate cross-contamination of samples between river transects. Each collection bottle will be rinsed three times with river water before filling with sample water. Approximately 1-liter of river water will be collected to satisfy the volume requirements for the metals analyses. Both filtered and unfiltered samples (note: unfiltered samples will be collected and analyzed to provide confirmation of the contaminant mass-balances) will be collected in the Buffalo River while only filtered water samples will be collected in the Saginaw River. Sample filtration will occur immediately after the water is collected. A 0.45 μm membrane filter will be used in the Buffalo River while a 0.50 μm Teflon filter will be used in the Saginaw River synoptic survey. Filters containing the particulate matter will be stored in precleaned polyethylene vials or precleaned aluminum foil envelopes and frozen (-20° C) for the Saginaw River and Buffalo River surveys, respectively. The contribution of contaminants bound on the particulate matter in the Buffalo River will be determined by subtraction of the

contaminants present in the filtered sample from those quantified in the unfiltered sample. Water samples collected for metals will be stored in polyethylene bottles. Water samples will be preserved by the addition of ultrapure nitric acid to reduce the pH to 2 or less. All water samples will be stored at 4 ± 2° C.

Water column sampling for organic analyses of pesticides, PCBs, and PAHs will require the collection of approximately 60-liters of river water. River water will be collected using the Sigma streamline pump sampler, or equivalent and will be collected in three 20-liter glass carboys. At each sampling station and depth, a portion of the samples will be pumped into each of the three carboys to approximate a composited sample in each carboy. After a transect has been sampled, the water will be transported to a clean room or laboratory where the water sample will be separated into two components, namely, the suspended particulate matter and a dissolved organic phase. The particulate matter will be isolated by passing the water sample through a penta-plate filter system containing ashed Whatman 293 mm GF/F filters. After filtration is complete, each filter is removed from the penta-plate and returned to a washed aluminum foil wraps. The dissolved organic phase will be isolated by drawing the filtered sample through a pre-prepared glass column containing XAD-2 resin. The filters and sealed XAD-2 columns will be placed in ice chests with the temperatures being maintained at 4 ± 2° C in the dark. As soon as possible after filtration, the filters will be frozen and stored at -20 ± 5° C until extraction and analysis.

Fish will be collected from the entire river within the AOC by electroshocking. Depending upon the availability of fish, some supplementary sampling with gill nets, trawls, and trap nets may be necessary. In the Buffalo River, carp will be collected and aged in the laboratory by scale analyses and divided into three age classes. Three samples of each age class will be taken, each sample being defined as the composite of five fish. A total of 45 fish will be taken to allow for further determination of the variability within a given age class. Stomach contents and muscle samples will be separated from each fish and shipped frozen (-20° C) to Battelle-MSL for subsequent analysis. In the Saginaw River, walleye, alewife, gizzard shad, and yellow perch will be collected and individually wrapped and stored frozen. These fish will be composited into groups of at least 5 fish and ground whole in the laboratory at the University of Michigan and 200 gram samples will be frozen and shipped to MSU for PCB analysis.

Additional samples will be collected at each site to provide water and particulates for miscellaneous limnological analyses. All the additional samples will be collected using the Sigma streamline pump sampler or an equivalent system. Limnological analyses to be performed by the Saginaw River team include determinations of alkalinity, hardness, suspended solid content, total organic carbon, and chlorophyll-a content, as well as the collection of zooplankton. Four liters of river water will be collected and stored in polyethylene bottles to satisfy these needs. Water samples will be filtered through a GF/C filter to separate the particulate fraction from the water sample. Filters will be stored frozen (-20 ± 5° C) while the water samples will be kept at 4 ± 2° C.

For the synoptic survey performed on the Buffalo River, additional samples will be collected for the determination of the following limnological parameters: sulfides, chlorides, TOC, dissolved organic carbon (DOC), hardness, alkalinity, and total suspended solids (TSS). Approximately 250

ml of water will be collected in amber glass bottles with teflon-lined polypropylene caps. These samples will be preserved with 4 drops of 2N zinc acetate per 100 ml of sample. Immediately after the addition of the zinc acetate, the pH of the samples will be checked and raised to a value greater than 9 through the addition of sodium hydroxide. Chloride and alkalinity analyses require the collection of 500 ml of water each in polyethylene bottles. TOC and DOC determinations require the preservation of the sample using H_2SO_4 to reduce the sample pH to 2 or less. Approximately 1 liter will be collected for the TOC and DOC analyses in amber glass bottles with subsequent analyses on both filtered (using pre-washed 0.45 μm glass fiber filters) and unfiltered samples. TSS analyses will require the collection of 1 liter of water in a polyethylene bottle. All the samples for the limnological parameters to be determined on the Buffalo River will be maintained at 4 ± 2° C.

The final sampling effort of the RA/M workgroup to support the mini-mass balance/synoptic surveys will be the collection of the CSOs on the Buffalo River. CSO sampling will be undertaken by field teams from SUC-B and the Buffalo Sewer Authority. Grab samples will be obtained using the Sigma streamline pump sampler that was used in the river survey. Flow velocity of the combined sewage will be measured subsequent to sampling using electric flow meters so that discharge and pollutant loadings can be determined. Grab samples will be collected by lowering the pump sampler intake through the street-level manhole into the flow. Additionally, an automated sampler will be placed at one of the selected CSOs. The automated sampler will collect a flow-proportioned sample to provide a best estimate of the "average" pollutant concentration and will be used to provide preliminary data for loading estimates. At least two additional storm overflow events will be monitored using the automated station. Correlations between the data generated from the grab samples and from the automated station sampling will be performed to determine if the two types of data can be used together in the modeling efforts. The collection of the CSO samples will follow the same sampling protocols as described for the river survey.

4.1.2.2 River Characterization Studies

In addition to the two synoptic surveys, two river characterization studies will be conducted by the RA/M workgroup. The first characterization study involves the determination of the resuspension potential of sediments while the second study involves the collection of TSS and other limnological data.

The sediment resuspension project will be performed under the direction of Dr. Wilbert Lick of the Department of Mechanical and Environmental Engineering from the University of California at Santa Barbara, Santa Barbara, California. Yaojun Xu and Joe McNeil will be responsible for the field work. This study basically involves resuspending the bottom sediments with a shaker. Two different shear stresses will be applied to the sediment at 8 to 12 different sites within the AOC. At least 4 of the sites will be located in deep water (greater than 10 feet deep) and at least 4 in shallow water (less than 10 feet deep). Sites will be selected from predominantly muddy bottom areas after consultation with the field crew from LLRS that has collected the T/C workgroup master and reconnaissance stations.

At each selected site for the resuspension study, the location of the site will be determined using the global positioning system or the Loran C navigation system. Sediment cores will be obtained by diver or by pole from on board ship. Cores will have 11.7 cm diameters and contain approximately 5 to 10 cm of sediment. The cores will then undergo the resuspension testing. Additional samples will be collected in polyethylene bottles for particle-size analysis. No sample preservation is required for particle-size analysis.

The New York State Department of Environmental Conservation (NYSDEC) will be responsible for conducting the second study. This study involves the collection of TSS data and other miscellaneous limnological parameters such as water temperature, conductivity, and water velocity (to be used to calculate discharge rates) on the Buffalo River. Simon Litten of the NYSDEC office in Albany, New York will be the principal investigator and John McMahon of the NYSDEC Region 9 office will be in charge of the sampling operations.

Samples to be collected for the second study will concentrate on high flow events with discharges of 6000 cubic feet per second at the river mouth. Discrete point samples will be taken with a P-72 point integrating sampler if water velocities are high enough to prevent the deployment of a Van Dorn sampler. Samples will be collected at 0.2 and 0.8 times the depth of the water at the sampling station. Similar to the circumstances of the synoptic surveys, thermal stratification is a concern at the mouth of the Buffalo River. If stratification exists, samples will be collected at 0.2 and 0.8 times the depth of each stratum. Stratification will be determined on the basis of temperature and conductivity profiles with depth. Temperature and conductivity measurements will be made in the field using a HydroLab Surveyor II® unit. Water velocities will also be determined at each site using the standard Gurley meter. The total water required for TSS measurements is approximately 0.4 liters. No special sample preservation techniques or bottle types are required for TSS analyses.

4.1.3 Engineering/Technology Workgroup Field Operations

The E/T workgroup's field operations will include the collection of bulk sediments to be used and distributed to various laboratories during the testing of the selected sediment remedial technologies. Sample collection is the responsibility of the USACE division or district offices for the Buffalo River, Grand Calumet River/Indiana Harbor, and Saginaw River/Bay AOCs. Samples to tested for remediation potential from the Ashtabula River and Sheboygan Harbor will be collected as part of the ongoing Superfund effort. Site locations will be marked on USACE sounding charts after determination via triangulation. Bulk samples will be collected from the toe of the channel using a crane barge bucket operation. Approximately 1 to 3 cubic yards of sediment will be retrieved per bucket. Sediments will then be scooped or shoveled from the bucket, working from top to bottom, to fill the appropriate number of 5 gallon plastic buckets. Approximately 100 gallons will be collected from each selected area within each AOC except for the potential resampling of a "hot spot"/master station on the Saginaw River, in which only 50 gallons will need to be collected. Samples will be shipped to ERL-D by motor freight at ambient temperatures. Degradation of organic compounds is not a major concern during shipping since these compounds are highly resistant to breakdown

and will be requantified prior to any treatment study being performed on the sediment. Sample compositing and homogenization will be performed at ERL-D using a cement mixer. Sediments will be deemed homogeneous by visual inspection of texture, color, and water content. After homogenization, samples will be stored at 4 ± 2° C in the dark.

4.2 Analytical Laboratory Operations

The sample analysis will be conducted through contracts/grants/interagency agreements to numerous analytical laboratories. This section will identify the general laboratory operations that will be required of all laboratories participating in the ARCS program. All analytical laboratories that have been identified at this time, the PIs responsible for the analysis and reporting of the final data, and which parameters will be analyzed by their laboratories will be presented. The prescribed methodologies to be used in the ARCS program will be presented (Table 2) and exceptions, with explanation, will be discussed, where known. If standardized methods or method references are not available, the PI will be responsible for having a written standard operating procedures (SOP) for the method available for review either in the QAPjP or during a laboratory system audit (to be discussed). Detailed analytical laboratory operations will be presented in the QAPjP that each participating laboratory is required to prepare for the ARCS program.

All laboratories participating in the ARCS program will be expected to follow good general laboratory practices as they relate to sample handling and tracking, filter preparation, sample preparation, instrument operation, bottle washing, storage and preparation of standards, etc. For laboratories performing bioassays, bioaccumulation studies, and/or fish tumor and abnormality studies, good general laboratory practice relating to animal health care (i.e., handling, feeding, and testing) will also be followed. SOPs related to these points will be available for inspection in the written QAPjP and/or during laboratory system audits.

For the ARCS program, required containers (i.e., glass, polyethylene) and lids (i.e., teflon-lined), preservation techniques, and holding times for collected samples will follow the protocols established in USEPA SW-846 (USEPA, 1986). Holding times at the laboratory will begin upon receipt of the samples from the field sampling crews. It is recognized that although as much as a week may pass since the samples were collected at the AOC, the analytical laboratories will not be held responsible for the elapsed time.

Initial instrument calibration, where appropriate, for all analyses performed in the ARCS program should be completed using a minimum of a three point curve or following the instrument manufacturer's instructions. The acceptance criteria for the initial three point calibration curve, where used, is that all points used in the determination of the calibration curve should have a calculated coefficient of determination (R^2) of ≥ 0.97. All instruments used in the ARCS program must be calibrated prior to analysis of any ARCS samples.

Table 2. Preferred and alternate methods accepted for analyses in the ARCS program[a].

Parameter	Preferred Method[b]	Alternate Methods[b]	Reference(s)[c]
Metals			
preparation$_{sediment}$	3050	200.4	USEPA, 1986 | USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
preparation$_{tissue}$	200.3		USEPA, 1990
Ag	7761	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
As	7061	XRF[d]	USEPA, 1986 | Nielson and Sanders, 1983
Ba	7081	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Cd	7131	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
Cr	7191	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Cu	7211	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Fe	7381	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Hg	7471	7470	USEPA, 1986 | USEPA, 1986
Mn	7461	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
Ni	6010	200.7	USEPA, 1986 | USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Pb	7421	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Se	7741		USEPA, 1986
Zn	7951	6010	USEPA, 1986 | USEPA, 1986
		200.7	USEPA, 1983
		XRF[d]	Nielson and Sanders, 1983
Organometals			
Methylmercury	GC/CVAF[d]		Bloom, 1989
Tributyltin	GC/FPD[d]		SOP[e]

Table 2 (cont.). Preferred and alternate methods accepted for analyses in the ARCS program[a].

Parameter	Preferred Method[b]	Alternate Methods[b]	Reference(s)[c]
Organics			
Dioxins/furans	8280		USEPA, 1986
PAHs[d] extraction	3540		USEPA, 1986
cleanup	3630		USEPA, 1986
analysis	8100	8310	USEPA, 1986 | USEPA, 1986
confirmation	8250	8270	USEPA, 1986 | USEPA, 1986
PCB[d]/congener extraction/cleanup	HPLC[d]		Krahn et al., 1988
analysis	GC/ECD[d]		NOAA, 1985
PCB[d]/aroclor extraction	3540		USEPA, 1986
cleanup	3620		USEPA, 1986
cleanup	3660		USEPA, 1986
analysis	8080		USEPA, 1986
Pesticides extraction	3540		USEPA, 1986
cleanup	3620		USEPA, 1986
cleanup	3660		USEPA, 1986
analysis	8080		USEPA, 1986
TOC/DOC[d]	9060	5310C combustion	USEPA, 1986 | APHA, 1985 SOP[e]
Water Quality Parameters[f]			
Alkalinity	310.1		USEPA, 1983
Conductivity	120.1	meter	USEPA, 1983 | Rhoades, 1982
Dissolved oxygen	360.1	360.2	USEPA, 1983 | USEPA, 1983
Hardness[g]	130.2	130.1	USEPA, 1983 | USEPA, 1983
Ca	7140	215.1	USEPA, 1986 | USEPA, 1983
Mg	7450	242.1	USEPA, 1986 | USEPA, 1983
Treatment Technology Parameters[h]			
Compressive strength	C 109-88		ASTM, 1987
Density			SOP[e]
Moisture content	D 2216-80		ASTM, 1987
Oil & Grease	9070	413.2	USEPA, 1986 | USEPA, 1983
SLT[d]			SOP[e]
TCLP[d]			40 CFR, 1987
Total inorganic carbon			SOP[e]
Total sulfur			SOP[e]

Table 2 (cont.). Preferred and alternate methods accepted for analyses in the ARCS program[a].

Parameter	Preferred Method[b]	Alternate Methods[b]	Reference(s)[c]
Miscellaneous Parameters			
Ammonia	350.3		USEPA, 1983
AVS[d]	GC/PID[d]		Cutter and Oatts, 1987
Chlorides	325.2	325.1	USEPA, 1983 | USEPA, 1983
Chlorophyll-a			Strickland and Parsons, 1972
Lipid content	gravimetric		Folch et al., 1957
Particle-size analysis	sieve/gravimetric	sieve/laser	SOP[e] | SOP[e]
pH	9045	150.1	USEPA, 1986 | USEPA, 1983
		meter	Plumb, 1981
Organohalogens	NAA[d]		SOP[e]
Solvent extractable residue	gravimetric		SOP[e]
Sulfides	376.2		USEPA, 1983
Total solids	160.3	208D	USEPA, 1983 | APHA, 1985
Total suspended solids	160.2	208D	USEPA, 1983 | APHA, 1985
Total volatile solids	160.4	209F	USEPA, 1983 | APHA, 1985

a - parameter groupings (e.g., metals, organometallics, etc.) are for organizational purposes only. Parameter group headings do not indicate a suite of parameters that are commonly analyzed together as a unit by the analytical laboratory. Parameter groupings analyzed for a given project are presented in Section 4.2.

b - where non-standard methods are used, a very brief description of the basic quantification technique is presented.

c - where multiple references appear on the same line and are separated by the symbol |, the first method listed is the reference for the preferred method while the second method listed is for the alternate method presented.

d - AVS = acid volatile sulfides; DOC = dissolved organic carbon; GC/CVAF = gas chromatography/cold vapor atomic fluorescence; GC/ECD = gas chromatography/electron capture detection; GC/FPD = gas chromatography/flame photoionization detection; GC/PID = gas chromatography/photoionization detection; HPLC = high pressure liquid chromatography; NAA = neutron activation analysis; PAH = polyaromatic hydrocarbons; PCB = polychlorinated biphenyls; SLT = serial leaching testing; TCLP = toxicity characterization leaching procedure; TOC = total organic carbon; XRF = X-ray fluorescence analysis.

e - SOP = standard operating procedure prepared by the analytical laboratory performing the specified analysis.

f - these parameters are generally associated with bioassays and fish bioaccumulation studies performed by the T/C and RA/M workgroups for the ARCS program.

g - hardness can either be determined by titration or through the determination and summation of Ca and Mg contents. Both results are presented as mg/L $CaCO_3$.

h - these parameters are generally associated with the tests performed by the E/T workgroup during remedial process testing for the ARCS program.

The samples received by the laboratories may or may not have undergone some form of homogenization by the parties responsible for their original collection and shipping. Subsequently, during shipment, the sample material within each container may segregate by particle-size, density, or some other related property. Therefore, all laboratories will be required to homogenize the samples prior to the removal of an aliquot for analysis. Homogenization can be performed either by manual or mechanized stirring of the sample in the bottle until visual homogeneity is obtained. A sample will be deemed visually homogeneous when no variation in color, water content, texture, etc. can be seen. All samples, extracts, pore waters, and standards for the ARCS program will be stored at 4 ± 2° C in the dark until extraction or final analyses unless otherwise specified. In cases where fish tissue, either whole fish homogenates or homogenates of various organs (i.e., stomach contents or muscle), samples will be maintained at -20 ± 5° C until extracted or digested for analysis. All temperature data will be kept in a bound logbook.

4.2.1 Toxicity/Chemistry Workgroup Laboratory Activities

Numerous chemical and biological parameters will need to be measured for the T/C workgroup to satisfy their goals established in section 2.3.3. In brief, the T/C workgroup is responsible for developing and testing sediment assessment methods through the determination of inorganic and organic chemistry parameters, bioassays (including benthic community structure determinations and mutagenicity tests), fish bioaccumulation studies, and fish tumor and abnormality surveys. The following text is divided into five sections, namely, inorganic chemistry, organic chemistry, bioassays, fish bioaccumulation assays, and fish tumors and abnormalities. For the bioassay and fish bioaccumulation sections, a discussion of water quality parameters that will be measured to ensure organism health prior to testing and to ensure that any toxic effects are due solely to the sediment, pore water, or elutriates during testing will be presented. It should be noted that physical parameter measurements, such as particle-size analysis and total solids, will be included in the discussion of inorganic chemical analyses.

4.2.1.1 Inorganic Chemistry

Inorganic chemical analyses will be performed on a variety of different media including pore waters, elutriates, sediments, and fish tissues for the T/C workgroup. Prior to the discussion of which parameters will be determined, the definition of the various media needs to be clearly stated. Pore water will be defined as the water separated from sediments strictly by centrifugation without the addition of extra water or chemicals. Pore water will therefore represent only the chemical phases that are in equilibrium with the sediment and not sorbed onto the sediment. Elutriates will be prepared from a 4:1 water:sediment (v/v) mixture that has been shaken, allowed to settle, and filtered to remove any remaining suspended particles. The elutriates will represent the water extractable phase of the chemical contaminants. Sediments will be simply defined as the solid phase material in a given sample.

As mentioned in the project description, Battelle-MSL will be one of the two primary laboratories used in the determination of inorganic chemical analyses for the T/C workgroup. The

Battelle-MSL operations for the ARCS program will be under the direction of Dr. Eric A. Crecelius. Battelle-MSL will perform chemical analyses on sediments collected from the master stations, pore waters and sediment elutriates prepared and shipped from NFCRC, and tissue samples as a result of the fish bioaccumulation studies.

The second laboratory used in the determination of inorganic chemical analyses for the T/C workgroup will be LLRS. The LLRS laboratory operations for the ARCS program will be under the direction of Dr. Michael D. Mullin. LLRS will perform both chemical and physical analyses on sediments collected at the reconnaissance stations as well as elutriates prepared from the sediments.

Inorganic chemical parameters to be analyzed for the T/C workgroup include the following parameters:

- Metals including Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn,
- pH,
- Ammonia,
- Total and volatile solids,
- Conductivity,
- AVS,
- Organometals (methylmercury and tributyltin),
- Lipid content,
- Solvent extractable residue,
- Organohalogens (Cl, Br, and I), and
- Particle-size analysis.

Battelle-MSL will perform analyses for Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Zn, AVS, and the organometals as well as determining lipid content from the fish tissue samples. LLRS will perform analyses for Cd, Cr, Cu, Fe, Ni, Pb, Zn, pH, ammonia, conductivity, organohalogens, solvent extractable residue, and particle-size analysis.

For the ARCS program, metals analysis, excluding Hg, should be performed using a hot nitric/hydrochloric acid digestion of the sediment (USEPA, 1986; SW-846 method 3050). Water matrices (e.g., pore water or from the water column) and elutriates may be aspirated with no additional preparation other than sample preservation with nitric acid to a pH <2.0. Fish tissues will be digested following USEPA (1990) method 200.3 for subsequent metals analysis. Quantification of the metals should be done by inductively coupled plasma (ICP) spectroscopy (USEPA, 1986; SW-846 method 6010) or graphite furnace atomic absorption (GFAA) spectroscopy (USEPA, 1986; SW-846 method 7000 or USEPA, 1983; method 200.7) or their equivalents. GFAA is the preferred method for metals quantification. Alternately, As and Se may be quantified using SW-846 methods 7061 and 7741 (USEPA, 1986), respectively, which employ gaseous hydride generation techniques. Mercury analysis should be performed by cold vapor atomic absorption (CVAA) following SW-846 method 7471 (USEPA, 1986). Alternate methods to those described here must first meet the approval of the ARCS QA Officer and T/C workgroup.

One known exception to the prescribed metal analytical procedures is that Battelle-MSL will digest the sediment samples using a nitric, perchloric, and hydrofluoric acid regime in a teflon pressure vessel. This analysis follows USEPA (1983) method 200.4. Quantification of the metals will be performed using the GFAA method as described above. The resultant digest will produce the total elemental contents for the metals while the nitric/hydrochloric digestion will yield the quantities of extractable metals (all the metals excluding the intercrystalline metals). Energy-dispersive X-ray fluorescence (XRF) analysis of undigested sediment samples will also be used during the quantification of total elemental metal contents by Battelle-MSL following the methods of Nielson and Sanders (1983).

The determination of pH of sediments will be done electrometrically using a pH probe and meter system following the method described by Plumb (1981), USEPA SW-846 method 9045 (USEPA, 1986), or USEPA method 150.1 (USEPA, 1983). Ammonia content of the elutriate will be determined potentiometrically using an ion selective probe and meter following USEPA method 350.3 (USEPA, 1983) or equivalent. Ammonia determination at LLRS laboratory will be performed following the instrument's instruction manual. USEPA methods 160.3 and 160.4 (USEPA, 1983), or their equivalents, will be used in the determination of total and volatile solids, respectively. Total and volatile solids will be determined gravimetrically after sample drying at 60° C and ashing at 550° C, respectively. Conductivity of the pore water will be determined following USEPA method 120.1 (USEPA, 1983) by measuring the specific conductance of the pore water at 25° C. LLRS will determine conductivity using the method of Rhoades (1982) which is an equivalent method.

The following methods do not, at this time, have a standardized USEPA approved methodologies. Laboratories employing these methods will be required to provide written SOPs or provide a published reference for the method. Acid volatile sulfides analysis will be performed following the method described by Cutter and Oatts (1987). This method basically involves the selective generation of H_2S in an acidic regime and subsequent gas chromatography (GC)/photoionization detection. Methylmercury and tributyltin (organometals) will be determined following SOPs developed at Battelle-MSL. Methylmercury will be analyzed in sediment, water, and tissue by ethylation followed by cryogenic GC with cold vapor atomic fluorescence detection (Bloom, 1989). Butyltin species will be determined in environmental samples by solvent extraction, followed by hexylation and quantification by GC with flame photometric detection. Lipid contents of the fish tissue submitted to Battelle-MSL from the NFRC-GL will be determined by the chloroform-methanol extraction procedure of Folch et al. (1957) and gravimetrically quantified.

Solvent-extractable residue (SER) will be determined gravimetrically from whole sediment after extraction with dichloromethane in a mixed sediment/anhydrous sodium sulfate mixture. The SER analyses will be performed at LLRS. The extracted samples will then undergo analysis for organohalogen content by neutron activation analysis (NAA). In brief, NAA measures organically-bound halogen concentrations by measuring the characteristic gamma-ray energy spectrum emitted by neutron-bombed elements.

Particle-size analysis will be performed at LLRS on sediment samples gravimetrically after separating the sample into five fraction via sieve analysis. The fractions will be divided at 1 mm,

250 μm, 63 μm, and 38 μm. The finest fraction (<38 μm) will be determined gravimetrically after sample aggregation, filtration, and drying at 105° C overnight.

4.2.1.2 Organic Chemistry

Four basic categories of organic compounds will be analyzed for the T/C workgroup, namely, pesticides, PCBs, PAHs, and dioxins/furans. Total organic carbon will also be determined to normalize the concentrations of the organic compounds in the samples. Organic chemical analyses will be performed on a variety of different mediums including pore waters, elutriates, sediments, and fish tissues.

The analysis of organic contaminants for the T/C workgroup will be the sole responsibility of Battelle-MSL. Table 3 provides a base listing of the organic compounds that will be looked for and quantified by Battelle-MSL. Organic analyses will be performed on sediments collected from the master stations, pore waters, and tissue samples as a result of the fish bioaccumulation studies as well as sediment elutriates prepared and shipped from NFCRC.

A majority of the organic compounds will be analyzed following the protocols established in USEPA SW-846 (USEPA, 1986). Pesticides and PCBs will be extracted following method 3540 (soxhlet extraction) and quantified following method 8080 which involves quantification by GC with an electron capture detector (ECD). Sample cleanup may be necessary to remove interferences and will follow method 3620 using a Florisil column and method 3660 to remove elemental sulfur from the sample. Congener-specific PCBs will be analyzed following the method of Krahn et al., (1988) and NOAA (1985), which involves a methylene chloride/anhydrous sodium sulfate extraction, a high pressure liquid chromatography (HPLC) carbon column cleanup, and quantification by GC/ECD. PAHs and chlorinated benzenes will be prepared by soxhlet extraction (method 3540) and quantified following method 8100. Concentrations of these compounds will be performed using a GC separation followed by flame ionization detector (FID). Secondary confirmation or the need to resolve PAH pairs may warrant the use of GC separation with mass spectroscopy (MS) quantification (methods 8250 or 8270). To remove interferences in the sample, the use of a silica gel cleanup will be used following method 3630. Dioxins and furans will be determined following method 8280 which involves the use of a high-resolution capillary column gas chromatography/low-resolution mass spectrometry technique. Sample cleanup procedures will be dependant upon the matrix and analytes to be quantified.

Total organic carbon will be analyzed by both LLRS and Battelle-MSL using an CHN analyzer that employs sample combustion to liberate carbon dioxide which is subsequently quantified by a thermal conductivity detector. TOC will be performed following the LLRS laboratory SOP which will be provided in their QAPjP for the ARCS program. At Battelle-MSL, TOC will be measured in a similar manner as at LLRS except following the protocols established in USEPA SW-846 (USEPA, 1986) method 9060.

Table 3. Organic compounds to be identified and quantified for the ARCS program.

Pesticide/Aroclor PCBs	PCB Congeners	PAHs and Chlorinated Benzenes	Dioxins/Furans
Aldrin	2,4'-dichlorobiphenyl	1,4-Dichlorobenzene	2378-TCDF
α-BHC	2,2',5'-trichlorobiphenyl	Naphthalene	Total TCDF
β-BHC	2,4,4'-trichlorobiphenyl	2-Methylnaphthalene	2378-TCDD
Δ-BHC	2,2',3,5'-tetrachlorobiphenyl	Dimethyl Phthalate	Total TCDD
Chlordane	2,2',5,5'-tetrachlorobiphenyl	Dibenzofuran	12378-PeCDF
4,4,DDD	2,3',4,4'-tetrachlorobiphenyl	Fluorene	23478-PeCDF
4,4,DDE	3,3',4,4'-tetrachlorobiphenyl	Phenanthrene	Total PeCDF
4,4,DDT	2,2',4,5,5'-pentachlorobiphenyl	Anthracene	12378-PeCDD
Dieldrin	2,3,3',4,4'-pentachlorobiphenyl	Fluoranthene	Total PeCDD
Endosulfan I	2,3',4,4',5-pentachlorobiphenyl	Pyrene	123478-HxCDF
Endosulfan II	3,3',4,4',5-pentachlorobiphenyl	Butylbenzylphthalate	123678-HxCDF
Endosulfan sulfate	2,2',3,3',4,4'-hexachlorobiphenyl	bis-(2-ethylhexyl)phthalate	123789-HxCDF
Endrin	2,2',3,4,4',5'-hexachlorobiphenyl	Chrysene	234678-HxCDF
Endrin aldehyde	2,2',4,4',5,5'-hexachlorobiphenyl	Di-n-Octylphthalate	Total HxCDF
Heptachlor	2,2',3,3',4,4',5-heptachlorobiphenyl	Benz(a)anthracene	123478-HxCDD
Heptachlor epoxide	2,2',3,4,4',5,5'-heptachlorobiphenyl	Benzo(b)fluoranthene	123678-HxCDD
Lindane (-BHC)	2,2',3,,4',5,5',6-heptachlorobiphenyl	Benzo(k)fluoranthene	123789-HxCDD
Toxaphene	2,2',3,3',4,4',5,6-octachlorobiphenyl	Benzo(a)pyrene	Total HxCDD
PCB 1016	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	Indo(1,2,3-cd)pyrene	1234678-HpCDF
PCB 1221	Decachlorobiphenyl	Benzo(ghi)perylene	1234789-HpCDF
PCB 1232			Total HpCDF
PCB 1342			1234678-HpCDD
PCB 1248			Total HpCDD
PCB 1254			OCDF
PCB 1260			OCDD

4.2.1.3 Bioassays

To examine the toxicity of the sediments and its pore water, as well as the potential toxicity of the sediment from elutriates to living organisms in the Great Lakes, numerous bioassays will be performed on the sediments from the master stations as well as Microtox™ being performed on sediments from the reconnaissance stations at LLRS. Discussion of bioassay testing will be divided into two parts, namely, the actual bioassay and the water quality parameters. Water quality parameters are important and used to ensure that the response seen in the test organism was due exclusively to the contaminants and not to organism stress from the culture or laboratory water used during testing. Each of these two topics will be addressed separately in this section.

The primary laboratories involved in the bioassay and toxicity testing are Michigan State University in East Lansing, Michigan, the National Fisheries Contaminant Research Center in Columbia, Missouri, and Wright State University in Dayton, Ohio. Each of the laboratories involved in the bioassay testing program and which tests will be performed at their laboratories will be presented in the following text.

The efforts of the USFWS NFCRC will be under the direction of Dr. Christopher G. Ingersoll. NFCRC will be performing the following bioassays on elutriates prepared from a 4:1 water:sediment mixture:

- Daphnia magna,
- Microtox™, and
- Selenastrum capricornutum.

Daphnia magna will be exposed to a sediment elutriate dilution series in a 48 hour test. Selenastrum capricornutum will also be exposed to a dilution series of sediment elutriates using 24 hour carbon fixation (^{14}C accumulation) test. Microtox™ will be applied in a 15 minute sediment elutriate toxicity test.

Solid phase testing on the sediments at NFCRC will be conducted for the amphipod Hyalella azteca and two midge species, Chironomus tentans and Chironomus riparius. Amphipod tests start with juvenile animals (<3rd instar) and may continue up to 28 days until reproductive maturation. Chironomus tentans tests start with second instar larvae (10 day old) and continue for 10 days until the fourth instar larval stage. Chironomus riparius tests start with first instar larvae (<24 hours old) and may continue up to 28 days through adult emergence.

NFCRC testing will also include the use of chemical extracts (extracted by Battelle-MSL in methylene chloride, subjected to gel permeation chromatography, and transferred into DMSO) obtained from sediment samples to assess any mutagenic activity using the Ames Salmonella microsome test. Four strains of Salmonella will be exposed to varying doses of sediment extracts in the presence and absence of rat liver S9. Mutagenic activity is indicated when the number of colonies on test plates is $\geq$ 2 times the number of spontaneous revertants on negative control plates.

Benthic community structure will be determined at NFCRC. All collected invertebrates will be taxonomically identified to the lowest possible classification. A multivariate approach in the analysis of invertebrate species abundance and biomass will be incorporated into a factor analysis of the resultant data. Principal component analysis will be used to help determine the underlying variance in species relative abundance. Shifts in "clusters" of species as a function of both physical and chemical differences in their habitat, provide information on the integrated response of aquatic communities to contaminants.

Tests being performed with Daphnia magna, Selenastrum capricornutum, Hyalella azteca, Chironomus riparius, and Chironomus tentans will follow the USEPA (1985, 1989) and ASTM (1989) toxicity test methods. Microtox™, Ames mutagenicity testing, and benthic community structures will be performed following written SOPs provided in the QAPjP. The last three test methods have undergone peer-review and have been published in scientific periodicals.

A majority of the bioassay testing will be performed under the direction of Dr. G. Allen Burton at WSU. Dr. Burton will be responsible for the collaboration of five universities and/or organizations who will be performing the actual bioassays. The collaborating investigators include the Illinois Natural History Survey (INHS) in Champaign, Illinois, the University of Minnesota in St. Paul, Minnesota, Memphis State University in Memphis, Tennessee, NOAA - Great Lakes Environmental Research Laboratory in Ann Arbor, Michigan, and WSU. The individual tests, the parties responsible for running the bioassay, the test length and endpoints, and the test media are presented in Table 4.

Toxicity test methods will adhere to USEPA (1985, 1989) protocols for testing of Pimephales promelas, Daphnia magna, Ceriodaphnia dubia, and Selenastrum capricornutum. Methods for the toxicity testing using Hyalella azteca, Lemna minor, and microbial activity assays will be presented as SOPs in the submitted QAPjP. These methods will follow previously reported methodologies in peer-reviewed periodicals. The methods for the remaining bioassay tests will be presented as SOPs in the submitted QAPjP.

Bioassays to be performed at MSU will be under the direction of Dr. John P. Giesy. MSU will be running bioassays using Ceriodaphnia dubia, Daphnia magna, Pimephales promelas, Selenastrum capricornutum, Chironomus tentans, and Microtox™. Two media will be used during the bioassays at MSU, namely, pore water and sediment. Pore water testing using Ceriodaphnia dubia, Daphnia magna, and Microtox™ tests will be performed to try to determine the efficiency and effectiveness of the use of pore water for bioassays as compared to using whole sediment for predicting toxic responses. Assays being performed with Ceriodaphnia dubia, Daphnia magna, Pimephales promelas, Selenastrum capricornutum, and Chironomus tentans will follow the USEPA (1985, 1989) and ASTM (1989) toxicity test methods. Microtox™ testing will be performed following methods that have undergone peer-review and have been published in scientific periodicals. Written SOPs will be provided in the QAPjP or be available for inspection during a laboratory system audit.

Table 4. Bioassays to be performed as a collaborative effort under the direction of WSU.

Assay Organism/Community[a]	Length of Test	Endpoint	Test Medium[b]	Responsible Party[c]
Pimephales promelas	7 day	Larval growth	S, E	WSU
Pimephales promelas	7 day	Embryo survival	S, E	WSU
Daphnia magna	48 hour	Survival	S, E	WSU
Daphnia magna	7 day	Survival/Reproduction (3 brood)	S, E	WSU
Ceriodaphnia dubia	7 day	Survival/Reproduction (3 brood)	S	WSU
Hyalella azteca	7 day	Survival	S	WSU
Hyalella azteca	10 day	Survival	S	WSU
Panagrellus redivivus	96 hour	Survival	E	INHS
		Development		
Pontoporeia hoyi	20 day	Survival	S	NOAA
		Avoidance		
		Uptake		
Hexagenia limbata	10 day	Survival	S, E	U. Minn.
		Molting Frequency		
		Uptake		
Selenastrum capricornutum	96 hour	Growth	E	WSU, INHS
	24 hour	^{14}C uptake	E	
Lemna minor	4 day	Growth (frond number)	E	WSU
		Chlorophyll-a	E	
Hydrilla verticillata	14 day	Chlorophyll-a	S	Memphis
		Dehydrogenase Activity	S	
		Shoot Length	S	
		New Growth	S	
Microtox™	15 minute	Luminescence	E	INHS
Alkaline phosphatase	2 hour	Enzyme Activity	S, E	WSU
Dehydrogenase	2 hour	Enzyme Activity	S, E	WSU
β-Galactosidase	2 hour	Enzyme Activity	S, E	WSU
β-Glucosidase	2 hour	Enzyme Activity	S, E	WSU
Rapid Bioassessment II,III	28 day	Community Indices (10)	S	WSU

a - Alkaline phosphatase, dehydrogenase, β-galactosidase, and β-glucosidase are all part of the bacterial activity as described in the project description.

b - S = sediment; E = elutriate.

c - U. Minn. = University of Minnesota; Memphis = Memphis State University.

The bioassays to be performed at MSU using Ceriodaphnia dubia and Daphnia magna as test organisms will be run for 48 hours with an endpoint of organism survival. Daphnia magna will also be tested in pore waters for 7 days to again test for survival but also for organism fecundity. Chironomus tentans bioassays will be performed for 10 days on the sediment noting survival and growth. Pimephales promelas testing for survival and, ultimately, bioaccumulation of contaminants will be assayed for 28 days. Microtox™ will be performed for the standard 15 minutes in a serial dilution series examining bioluminescence as an endpoint. Selenastrum capricornutum will be tested in a serial dilution series for 24 hours noting ^{14}C uptake.

Microtox™ testing on elutriates from the reconnaissance stations will be performed at LLRS. The Microtox™ test will be performed following the SOP provided to LLRS from NFCRC, thereby, maintaining comparability among the laboratories performing the same bioassay test.

Water quality parameters in bioassay testing will be used to ensure organism health prior to exposure to contaminants in the sediments, elutriates, or pore waters. Further, water quality parameters will be used to ensure that the responses identified in the organisms are due entirely to the contaminants in the sample. Water quality parameters include:

- Hardness,
- Alkalinity,
- Dissolved oxygen (DO),
- pH,
- Conductivity, and
- Temperature.

Additional water quality parameters such as ammonia, chloride, sulfate, and turbidity may be monitored at the discretion of the PI if these parameters are a concern at their laboratory. Light intensity and photoperiod, where appropriate, will be monitored during each bioassay at all laboratories participating in the ARCS program.

Water quality parameter measurements will be made following USEPA test methods (1983) or following the instrument manufacturer's instructions unless otherwise cited. Hardness will be tested following method 130.2, or equivalent, which involves the sample titration after Ca and Mg complexation using ethylenediamine tetraacetate (EDTA). Alkalinity, a measurement of the water's capacity to neutralize acid, will be determined by titration to an endpoint of pH = 4.5 will follow method 310.1 or equivalent. Dissolved oxygen will be measured electrometrically using a probe (method 360.1) or using a modified Winkler procedure (method 360.2). Measurement of pH will be performed using a pH electrode following USEPA (1983) method 150.1, USEPA (1986) SW-846 method 9045, manufacturer's instruction, or their equivalents. Conductivity, a measure of the electrical conductance within a sample, will be tested using a self contained conductivity meter employing USEPA (1983) method 120.1 or equivalent. Temperature will be measured using either NIST (National Institute of Standards and Technology, formerly the National Bureau of Standards - NBS) traceable thermometer or using a temperature probe. Due to the simplicity of this measurement, no standard method needs to be followed for the ARCS program.

4.2.1.4 Fish Bioaccumulation Assays

Fish bioaccumulation assays will be performed as part of the ARCS program to assess the buildup of contaminants in fish tissue due to exposure to contaminated sediments. Ten day tests using Pimephales promelas as the test organism will be performed at NFRC-GL under the direction of Dr. John E. Gannon. A 28 day bioaccumulation assay using Pimephales promelas will be performed at MSU under the direction of Dr. John P. Giesy. Water quality parameters will be monitored during these assays following the methods/techniques presented in the bioassay section (section 4.2.1.3). Quantities of accumulated contaminants in the fish tissues will be determined at Battelle-MSL following the procedures presented in sections 4.2.1.1 and 4.2.1.2.

4.2.1.5 Fish Tumor and Abnormalities

The NFRC-GL, under the direction of Dr. John E. Gannon, will conduct surveys of tumors and other physical abnormalities in bottom fish from the Grand Calumet River. Types and incidences of tumors will be determined on the brown bullhead (Ameiurus nebulosus), preferably, after field necropsy and preservation of tissues and histological examination. If brown bullheads are not found, or are in insufficient number, the white sucker (Catostomus commersoni) will become the target species of bottom dwelling fish. Biological data such as external abnormalities, age, sex, and size will also be obtained from the sampled fish.

4.2.2 Risk Assessment/Modeling Workgroup Laboratory Activities

Numerous chemical parameters will need to be measured for the RA/M workgroup to satisfy their goals established in section 2.3.4. The RA/M workgroup laboratory activities will be geared towards providing data for the mini-mass balance synoptic surveys as described in section 2.3.4 and various modeling efforts such as the hydrodynamic, sediment transport, and food chain models. Additionally, as a preliminary evaluation of sediment toxicity and potential contamination, TIE will be performed on the sediments.

Toxicity identification evaluation analyses and bioassays will be performed at ERL-D under the direction of Dr. Gerald T. Ankley and at WSU under the direction of Dr. G. Allen Burton. TIE basically involves the manipulation of the extracted pore waters from the sediments followed by toxicity testing. The manipulations of the pore water are intended to change the toxicity of the sample. These manipulations include:

- A baseline test,
- pH adjustment to pH 3 and 11,
- pH adjustment and aeration,
- pH adjustment and filtration,
- pH adjustment and solid phase extraction through C18 columns,
- EDTA chelation,
- Oxidant reduction, and
- Graduated pH testing.

Bioassays are subsequently performed on the manipulated pore waters, after being adjusted back to their initial pH values (except in the graduated pH test in which no readjustment of the pore water will be made), using Pimephales promelas and Ceriodaphnia dubia as test organisms.

Bioassays using Pimephales promelas and Ceriodaphnia dubia will be performed following protocols defined by the USEPA (1985, 1989) or their equivalents. Pimephales promelas testing will occur for up to 96 hours in a serial dilution test monitoring organism survival. Ceriodaphnia dubia testing will monitor survival during a 48 hour period in a serial dilution test.

During the bioassay testing, the water quality parameters of hardness, pH, conductivity, and DO will be monitored to ensure that the identified organism response is due solely to the contaminants present in the sediment pore waters. Hardness will be measured either indirectly via titration following USEPA (1983) method 130.2, or its equivalent, or by direct measurement by flame atomic absorption spectrometry (AA) of calcium and magnesium following USEPA (1983) method 215.1 and 242.1, USEPA (1986) SW-846 methods 7140 and 7450, or their equivalents. Measurement of pH will be performed using a pH electrode following USEPA (1983) method 150.1, USEPA (1986) SW-846 method 9045, manufacturer's instruction, or their equivalents. Conductivity, a measure of the electrical conductance within a sample, will be tested using a self contained conductivity meter employing USEPA (1983) method 120.1 or equivalent. Dissolved oxygen will be measured electrometrically using a probe (USEPA, 1983; method 360.1 or equivalent).

ERL-D will also perform quantification of the ammonia content of the pore waters as well as the metals concentrations if the manipulation tests in TIE indicate that toxic effects are due to either of these two contaminants. Ammonia will be determined using an ion selective electrode following USEPA (1983) method 350.3 or equivalent. Metal concentrations of As, Cd, Co, Cr, Cu, Mn, Ni, and Zn will be quantified, after sample preservation to a pH <2 using concentrated reagent grade nitric acid, using GFAA (USEPA, 1986; SW-846 method 7000 or equivalent).

In support of the mini-mass balance synoptic survey efforts, chemical analyses will be performed on particulates (or suspended sediment) and waters from the Buffalo and Saginaw Rivers. The State University College at Buffalo in Buffalo, New York under the direction of Dr. Harish C. Sikka will conduct the analyses on the Buffalo River samples while the members of the Michigan Sea Grant College Program, under the direction of Dr. Russell A. Moll will conduct the sample analysis program for the Saginaw River. Each synoptic survey's laboratory activities will be discussed separately in the following text.

The parameters that will be examined in the Buffalo River priority consideration area by SUC-B include the following contaminants:

- Total PCBs,
- DDT,
- Dieldrin,
- Chlordane,
- Benzo(a)pyrene,

- Benzo(a)anthracene,
- Benzo(b)fluoranthene,
- Benzo(k)fluoranthene,
- Chrysene,
- Pb, and
- Cu.

All organic compounds will be analyzed following the protocols established in USEPA (1986) SW-846. Pesticides and PCBs will be quantified following method 8080 which involves quantification by GC/ECD. Sample cleanup may be necessary to remove interferences and will follow method 3620 using a Florisil column and method 3660 to remove elemental sulfur from the sample. PAHs (benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and chrysene) will be quantified following method 8100 or 8310. Concentrations of these compounds will either be performed using a GC separation followed by flame ionization detection or HPLC with a fluorescence detector. To remove interferences in the sample, the use of a silica gel cleanup will be used following method 3630.

Metals analysis will be performed using a hot nitric/hydrochloric acid digestion of the particulates (USEPA, 1986; SW-846 method 3050). Quantification of the metals will be done by GFAA following USEPA (1986) SW-846 method 7000, USEPA (1983) method 200.7, or their equivalents. GFAA is the preferred method for metals quantification for the ARCS program.

In addition to the contaminants previously discussed, a series of "conventional" river parameters will be measured for the Buffalo River waters. These conventional parameters include:

- Sulfides,
- Alkalinity,
- Hardness,
- Chlorides,
- TOC,
- DOC, and
- TSS.

Sulfides in the river water will be determined colorimetrically after reaction with dimethyl-p-phenylenediamine to produce methylene blue following USEPA (1983) method 376.2 or equivalent. Alkalinity will be determined by titration to an endpoint of pH = 4.5 will follow USEPA (1983) method 310.1 or equivalent. Hardness will be measured directly by flame AA of calcium and magnesium following USEPA (1983) method 215.1 and 242.1, USEPA (1986) SW-846 methods 7140 and 7450, or their equivalents. Chloride contents will be examined using the colorimetric/automated ferricyanide system (USEPA, 1983; method 325.2 or equivalent). The quantification of TOC and DOC will follow the protocols established in USEPA (1986) SW-846 method 9060 which involves the conversion of organic carbon, by combustion, to carbon dioxide and the subsequent detection and quantification of the CO_2 by an infrared detector. TSS will be determined gravimetrically after filtration and drying. USEPA (1983) method 160.2 or equivalent is appropriate for this analysis.

The contaminants to be analyzed in water and particulate samples collected in the Saginaw River AOC by MSG will be:

- Total PCBs,
- Pb,
- Fe,
- Cu, and
- Zn.

All four metals in the particulate fraction will be quantified after sample digestion using concentrated nitric acid and hydrogen peroxide (30%) and GFAA analysis (USEPA SW-846 method 7000, 1986, or equivalent). The method for sample digestion proposed by MSG is a variant on USEPA (1986) SW-846 method 3020 and should be acceptable for the ARCS program. A written SOP for this method will be available for review during a laboratory system audit. Filtered water samples will be tested for Cu, Pb, and Zn using GFAA techniques following USEPA (1986) SW-846 method 7000, or equivalent, after sample concentration by freeze-drying. A written SOP of the freeze-drying technique will be provided in the MSG QAPjP.

Total PCB contents will be determined on the XAD-2 resin column and the filter papers obtained from the field processing of the river waters. These samples will be extracted following USEPA (1986) SW-846 method 3540, or equivalent, which uses a Soxhlet extraction procedure. PCBs will be quantified following USEPA (1986) SW-846 method 8080 which involves quantification by GC with an electron capture detector (ECD). Sample cleanup may be necessary to remove interferences and will follow method 3620 using a Florisil column and method 3660 to remove elemental sulfur from the sample (USEPA, 1986). PCB concentrations in fish tissue and zooplankton samples will also be determined following these methods.

Similar to the synoptic survey to be performed on the Buffalo River, "conventional" river parameters, including determinations of alkalinity, hardness, TSS, TOC, and chlorophyll-a content, will also be determined by MSG. TSS will be determined gravimetrically after filtration and drying. TOC quantification will follow the protocols established in USEPA (1986) SW-846 method 9060 which involves the conversion of organic carbon, by combustion, to carbon dioxide and the subsequent detection and quantification of the CO_2 by an infrared detector. Alkalinity and hardness determinations will be made using USEPA (1983) methods 130.2 and 310.1, or equivalents, respectively. Chlorophyll-a contents will be performed employing the method described by Strickland and Parsons (1972).

Two additional studies that will be conducted to support the sediment transport modeling effort will be performed at UCSB and by the NYSDEC. Testing done by UCSB will be done under the direction of Dr. Wilbert Lick while work performed by the NYSDEC will be under the direction of Dr. Simon Litten. Both laboratories will be performing TSS quantification analyses. TSS will be determined following method 208D in Standard Methods (APHA, 1985), or equivalent. Particle-size analysis will be performed at UCSB using a combination of sieving for larger particles (> 0.25 μm)

and the Malvern particle-size analyzer for the finer fraction (512 to 1 μm). The remaining particle sizes will be determined by difference. Written SOPs will be available at the laboratory for inspection or will be provided upon request.

4.2.3 Engineering/Technology Workgroup Laboratory Activities

The primary laboratory activities of the Engineering/Technology workgroup will be to evaluate and test available removal and remedial technologies for contaminated sediments. The laboratory activities of the E/T workgroup can be divided into two sections, namely, preliminary sediment sample characterization and remediation process efficiency testing. Each of these categories will be discussed separately in the following paragraphs.

The basic preliminary characterization of the sediment will be performed by ERL-D and will include the following parameters:

- TOC,
- Total inorganic carbon (TIC),
- Particle-size distribution,
- Density of dry material,
- Total sulfur content,
- AVS,
- Oil and grease (O&G),
- Total PCBs,
- PAHs, and
- Metals including Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn.

Most of the methods used in the preliminary characterization of the sediments at ERL-D will follow protocols described in USEPA (1986) SW-846. Exceptions include the analyses of total inorganic carbon, particle-size, density, total sulfur, and AVS, for which written SOPs or references for these methods will be provided in the QAPjP submitted by ERL-D. TOC and O&G will be analyzed using methods 9060 and 9070, or equivalents, respectively. Total PCBs will be quantified following method 8080 which involves quantification by GC/ECD. Sample cleanup may be necessary to remove interferences and will follow method 3620 using a Florisil column and method 3660 to remove elemental sulfur from the sample. PAHs will be quantified following method 8100. Concentrations of these compounds will be determined using GC/FID. Secondary confirmation or the need to resolve PAH pairs may warrant the use of GC separation with mass spectroscopy quantification. To remove interferences in the sample, the use of a silica gel cleanup will be used following method 3630. Metals, including Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn, will be analyzed using a hot nitric/hydrochloric acid digestion of the sediment (method 3050) with the exception of Hg. Quantification of the metals should be done by ICP (method 6010) or GFAA (method 7000) or their equivalents. GFAA is the preferred method for metals quantification. Mercury analysis should be performed by CVAA following method 7471.

To satisfy the E/T workgroup's responsibilities numbers 8 and 10 (treatment technologies for inorganic contaminants and evaluation of solidification/stabilization technologies, respectively) as listed in the project description in section 2.3.5, two specific laboratories will be used to assess the efficiency of the remedial alternatives selected. A general description of the analytical laboratory activities required to satisfy E/T workgroup responsibility number 7 (bench-scale testing of selected treatment technologies) will be provided for those remedial techniques that degrade organic contaminants such as PCBs and PAHs.

The treatment technologies for the remediation of inorganic contaminants (task 8) will be the primary responsibility of the Bureau of Mines under the direction of Mr. James P. Allen. The BOM will examine the treatment options that include the extraction and recovery of metals from the contaminated sediments. Samples that are submitted to the BOM will undergo particle size separations prior to chemical analysis using a variety of techniques, such as sieving and cycloning, froth flotation, gravity separation, and magnetics. SOPs for the separation technologies will be available for inspection during laboratory system audits.

Metals to be quantified in the untreated and treated (or remediated), fractionated sediments include Ag, As, Ba, Cd, Cr, Hg, Pb, Sb, and Se. Metals analysis will be performed using a hot nitric/hydrochloric acid digestion of the sediment (USEPA, 1986; SW-846 method 3050) with the exception of Hg. Quantification of the metals will be performed by GFAA or flame AA (USEPA, 1986; SW-846 method 7000) or their equivalents. GFAA is the preferred method for metals quantification. Alternately, Se may be quantified using USEPA (1986) SW-846 method 7741, respectively, which employ gaseous hydride generation techniques. Mercury analysis should be performed by cold vapor atomic absorption following USEPA (1986) SW-846 method 7471.

WES under the direction of Mr. Daniel E. Averett will perform remedial tests on sediments from the Buffalo River employing chemical solidification/stabilization (CSS) techniques which are probably the most proven techniques for remediation of contaminated sediments. The scope of the study will involve laboratory preparation of CSS samples using sediment and one of the following binders/additives: portland cement, lime/fly ash, kiln dust, and portland cement with powdered activated carbon. A range of binder-to-sediment ratios will be screened and an optimal ratio will be selected for detailed evaluation. Effectiveness will be measured by comparing leaching results, unconfined compressive strength, and durability under multiple wet/dry and freeze/thaw cycles at WES.

Written SOPs for the wetting/drying and freezing/thawing test procedures will be provided in the WES QAPjP. The determination of unconfined compressive strength will be performed following ASTM (1987) method C 109-88. Two leaching procedures will be used at WES, namely, serial leaching test (SLT) and toxicity characterization leaching procedure (TCLP). TCLP will be performed following the method described in 40 CFR Part 268 (1987). A written SOP for the SLT will be provided in the WES QAPjP.

Upon the selection of the "ideal" binder-to-sediment ratio, bench scale testing will be performed in which the following chemical analyses will be performed to assess the methods efficiencies for the removal of contaminants from the system:

- Metals including Cr, Cu, Ni, Pb, and Zn,
- PAHs (including base, neutral, and acid extractables),
- pH,
- Conductivity,
- Moisture content,
- Total volatile solids, and
- O&G,
- TOC.

Metals to be analyzed at WES include Cr, Cu, Ni, Pb, and Zn. Metals will be extracted using nitric acid and hydrogen peroxide following USEPA (1986) SW-846 method 3050, or their equivalents. Quantification of Cr, Pb, Cu and Ni will be made using GFAA (USEPA, 1986; SW-846 methods 7191 and 7421 and USEPA (1983) methods 220.2 and 249.4, respectively). Zn will be analyzed by ICP following USEPA (1986) SW-846 method 6010.

PAHs will be quantified at WES following the protocols established in USEPA (1986) SW-846 method 8270 which utilizes a capillary column GC/MS technique. The measurement of pH and conductivity will also be performed following USEPA (1986) SW-846 methods 9040 and 9050, respectively. Moisture content and total volatile solids will be determined gravimetrically (ASTM, 1987; methods D 2216-80 and APHA (1985) Standard Methods 209F, respectively). USEPA (1983) method 413.2 will be used for the determination of O&G in the sediments. This method uses infrared spectrophotometric techniques in the quantification process. TOC will be analyzed using APHA (1985) Standard Methods 5310C using sample combustion followed by thermal conductivity detection of the released/generated carbon dioxide.

In general, for the remedial processes in the ARCS program that are aimed at the degradation of organic compounds such as pesticides, PCBs, and PAHs, a quantification of the concentrations of these compounds must be made prior to remediation and then after the remedial process. For the ARCS program, the quantification of these compounds should be performed using the following established protocols presented in USEPA (1986) SW-846. Pesticides and PCBs will be quantified following method 8080 which involves quantification by GC with an electron capture detection. Sample cleanup may be necessary to remove interferences and will follow method 3620 using a Florisil column and method 3660 to remove elemental sulfur from the sample. PAHs will be quantified following method 8100. Concentrations of these compounds will be performed using GC/FID methods. Secondary confirmation or the need to resolve PAH pairs may warrant the use of GC/MS quantification (methods 8250 or 8270). To remove interferences in the sample, the use of a silica gel cleanup will be used following method 3630.

4.3 Sample Custody

No formalized chain-of-custody is required for the ARCS program. Sample recipients will be notified by telephone of the number and identity of samples shipped at the time of shipment from LLRS or ERL-D, whichever source is appropriate. Sample recipients should in return, notify LLRS or ERL-D that the samples have been received and the condition of the samples received (i.e., if the samples leaked, broken bottle, etc.) in the event that additional sample is required by the analytical laboratory. Records will be maintained of sample collection dates, labeling, handling, transport, tracking, and laboratory analyses performed on the sediment samples at a given analytical laboratory.

Section 5

Quality Assurance Program

This section describes the QA program which is designed to allow both control and assessment of measurement uncertainty during the sampling, sample preparation, and analysis phases of the ARCS program.

5.1 Overview of Quality Assurance Objectives

The data collection criteria provide a balance between constraints of time and cost and the quality of data necessary to achieve the ARCS program research objectives. The ARCS QAPP is designed to accomplish the following objectives:

- Establish the QA/QC criteria used to control and assess data collection in the ARCS program,
- Provide comparable sampling, preparation, and analytical methods and procedures,
- Utilize assessment samples and procedures to verify the quality of the data,
- Perform field and on-site laboratory system audits to ensure that all activities are properly performed and that discrepancies are identified and resolved, and
- Evaluate the data and document the results in a final QA report to GLNPO management.

To aid in this effort, it is necessary to identify both qualitative and quantitative estimates of the quality of the data needed by the ARCS data users. Guidelines established by the USEPA Quality Assurance Management Staff (Stanley and Verner, 1985) encourage the data users to clearly identify the decisions that will be made and to specify the calculations, statistical and otherwise, that are to be applied to the data.

The raw data for the ARCS program will be collected during three major operational phases consisting of sediment mapping, sampling, and analysis. A certain amount of data measurement uncertainty is expected to enter the system at each phase. The sampling population itself is a source of confounded uncertainty that is extremely difficult to quantify. Generally, the data quality objectives encompass the overall allowable uncertainty from sample measurement and from the sampling population that the data users are willing to accept in the analytical results (Taylor, 1987). Because of the many confounding sources of uncertainty, overall DQOs for the ARCS program have not been defined.

This QAPP focuses on the definition, implementation, and assessment of measurement quality objectives that are specified for the entire sample preparation and analysis phases of data collection as well as for the verification of the field sampling phase. The MQOs are more or less specific goals defined by the data users that clearly describe the data quality that is sought for each of the measurement phases. The MQOs are defined according to the following six attributes:

- Detectability - the lowest concentration of an analyte that a specified analytical procedure can reliably detect,
- Precision - the level of agreement among multiple measurements of the same characteristic,
- Accuracy - the difference between an observed value and the "true" value of the parameter being measured,
- Representativeness - the degree to which the data collected accurately represents the population of interest,
- Completeness - the quantity of data that is successfully collected with respect to the amount intended in the experimental design, and
- Comparability - the similarity of data from different sources included within individual or multiple data sets; the similarity of analytical methods and data from related projects across AOCs.

Initial MQOs were established by the principal laboratories performing a given type of measurement (i.e., inorganic or organic analyses, bioassays, etc.) after discussion and approval by the members of the T/C and/or E/T workgroups. In most cases, if not all, the initial proposed QA program and MQOs were equivalent to the QA program routinely implemented at the analytical laboratory. Upon the initiation of the formal QA program within the ARCS program, the existing MQOs were either accepted or modified with additional requirements to ensure data quality in the ARCS program, where necessary. The resultant MQOs were then applied to all parameters in the process of being analyzed and to all future analyses. It will be these MQOs that will be reported in the remainder of this section. Discrepancies to the stated ARCS program MQOs will be described in the final QA report to be submitted to GLNPO by EMSL-LV and LESAT upon completion of the ARCS program.

If the data quality goals cannot be met during the course of the project, the actual level of quality will be used to reassess the intended use of the data. A lower than desired attainment of data quality could require different approaches to be used in data analysis or may result in modifications to the levels of confidence assigned to the data. These points will be addressed in the final QA report to be submitted to GLNPO by EMSL-LV and LESAT upon completion of the ARCS program.

5.2 Design Characteristics

An important part of the QA program for the ARCS program consists of the use of various QC samples. The QC samples enable the laboratory to control measurement error and meet the MQO requirements. In order to assess the MQOs, a series of different sample types must be analyzed together with the routine samples in a manner that is statistically relevant and in which conclusions concerning the quality of the data can be drawn.

In order to produce data of consistently high and known quality, the participating laboratories are required to analyze certain types of QC samples that are known to the laboratory staff and that

can be used by the analysts to identify and control analytical measurement uncertainty. Each QC sample has certain specifications that must be met before data for that parameter is considered acceptable. These specifications include acceptance limits and frequency of sample use requirements. The QC samples are non-blind samples to assist the laboratory in meeting laboratory MQOs and include sediment, sediment extracts (including pore water and elutriates), water column samples, and fish tissue samples, e.g., analytical replicates, as well as non-sediment, non-water, or non-fish tissue based samples, e.g., reagent blanks. The QC samples are analyzed by each laboratory and allow the PI and laboratory QA staff to assess whether the physical, chemical, and biological testing is under control.

The overall QA program presented is applicable throughout the ARCS program (i.e., for all three technical workgroups) and for all media (i.e., sediment, river water, pore water, elutriate, or fish tissue) in which the contaminants are to be investigated. The acceptance limits and frequency of use criteria may vary slightly between different workgroups, due to size of analytical batches and/or the usage of the resultant data, but the quality of the data for its intended use will not be compromised. For example, in the testing of a sediment that has undergone a remediation process that is supposed to remove organic compounds for the E/T workgroup, the accuracy, precision, and detection limits for the inorganic metals, monitored strictly for mass balance purposes, may not be as strict as for the analyses of metals performed for the T/C workgroup where sediment characterization is the workgroup's primary objective. Where these exceptions are known to exist, they will be noted in the appropriate section.

For the purposes of the following discussions, several definitions of a batch or sample set are required dependent upon the type of investigation being conducted. A batch or sample set for inorganic and organic chemistry parameters, excluding the analogous tests performed to indicate water quality for bioassays and bioaccumulation studies, will be defined as 20 or fewer routine samples to be analyzed for a given contaminant within a given medium. In other words, a batch being analyzed for PCBs in sediment and pore water extracted from the same sediment constitutes two different analytical batches even though they are from the same bulk sample. A different definition for a batch needs to be defined for the bioassays and fish bioaccumulation studies. A batch for these studies will be defined as all tests being performed simultaneously for a given assay in a given media (sediments, elutriates, or pore waters) from a given AOC. Fish tumor and abnormality survey batches will include all fish collected from a given AOC during a given sample collection trip.

The following sections will describe the types of QC samples, their acceptance limits, and required frequencies of use by parameter or parameter group (i.e., PCBs, PAHs, etc.) required in the ARCS program. Section 5.3 will discuss the quality assurance objectives of precision, accuracy, representativeness, comparability, and completeness.

5.2.1 Analytical Replicate Samples

A triplicate subsample of a routine sample is required for all inorganic and organic analyses with the exception of the inorganic analyses used to check water quality conditions during bioassays or fish bioaccumulation studies. For the water quality parameter testing used in conjunction with bioassay or fish bioaccumulation testing, duplicate analyses will be required. The selection of the replicate sample is to be at random from all the samples in a given batch. These samples will be used to ensure that within-batch precision MQOs are being satisfied (i.e., an estimate of the degree/extent of homogeneity obtained within the sample). Precision is calculated as a relative percent difference (RPD) or relative standard deviation (RSD) and is evaluated to ensure that the results are within acceptable limits set forth in this document (section 5.3) and submitted QAPjPs. If the precision objectives for the analytical replicate are not met, corrective actions should be initiated to determine the cause for the poor resultant precision. These corrective actions can include a recalculation of the data, recalculation of the RPD or RSD, reanalysis of the samples, and/or reanalysis of the entire sample batch. Notification of the laboratory QA officer should be done immediately upon identification of any problem.

For the bioassays and fish bioaccumulation studies, all samples to be tested are run in triplicate at a minimum. Routinely, four or more replicates of each sediment, pore water, or elutriate are tested per organism. Precision for the fish tumor and abnormality studies will be achieved by cross-checking approximately 10% of the samples by another fish pathologist.

One known exception to the use of triplicate analyses exists in the ARCS program. At the LLRS laboratory, duplicate analysis will be performed during the determination of the indicator parameters. These duplicate samples will be performed on one in every ten routine samples instead of once per batch. The more frequent, but less reliable, duplicate samples are required to maintain control of analytical measurement uncertainty during the processing of the numerous reconnaissance station samples collected during each reconnaissance and mapping survey.

5.2.2 Field Duplicate Samples

Field duplicate samples will be applied to the collection of reconnaissance station samples collected for the T/C workgroup and during the mini-mass balance synoptic surveys performed for the RA/M workgroup. During the collection of the reconnaissance stations, a duplicate core sample will be collected, described, and analyzed by LLRS on each sampling day. The duplicate cores will be collected by slightly moving the vibra-core unit and coring a separate sample. Duplicate water column, particulate, and CSO samples (where collected) will be collected during the synoptic surveys. Field duplicates will be collected at a rate of one duplicate per sampling day. Precision is calculated as a relative percent difference between the two samples for each analyzed parameter. Precision for the field duplicate should have an RPD of $\leq$ 30%. Individual pairs will be used to assess the overall within-batch precision and to provide the data user with an estimate of the natural variability in the distribution of contaminants within the sediments or other media sampled. These estimates will be pooled to provide the within-batch component of the overall system

measurement uncertainty. If the precision objectives for the field duplicates is not met, corrective actions should be initiated to determine the cause for the poor resultant precision. These corrective actions will be primarily based upon the recalculation of the data and recalculation of the RPD (to ensure proper calculations have been performed) due to the expected highly varied nature of the sediments. For the water column and particulate samples, however, reanalysis of the samples or reanalysis of the entire sample batch may be warranted after recalculations have been performed.

5.2.3 Reagent Blanks

For physical and chemical analytical methodologies that require sample preparation, a reagent blank for each batch of samples processed is prepared and analyzed. A reagent blank is defined as a sample composed of all the reagents, in the same quantities, used in preparing an actual routine sample for analysis. The reagent blank will undergo the same digestion and extraction procedures as an actual routine sample. For liquid samples, the reagent blank will be either distilled/deionized water or the combination of reagents used during extraction/digestion. For solid samples, the reagent blank will be the weighing dish or sample holder without the addition of any sediments. These reagent blanks are used to check for significant baseline drift and potential contamination within a batch of samples. The MQOs (presented in Table 5) for all reagents blanks in the ARCS program are that the blanks must have a measured concentration $\leq$ method detection limit (MDL). Reagent blanks are to be run at the beginning, middle, and end of the batch for inorganic analyses and at a rate of 1 per batch for organic analyses. If the MQOs for the reagent blanks are not met, a new reagent blank is to be prepared and analyzed. All samples associated with the "high" blank should be reprocessed and reanalyzed after the contamination source has been identified and eliminated.

During the bioassay and bioaccumulation studies, the "reagent blank" is better known as the control sample. This sample simply consists of the water in which the organisms have been either cultured or raised. Control samples can not be performed in solid phase (whole sediment) bioassays, due to the nature of these tests. Control samples should be assayed at a rate of at least one per sample batch. The control sample in these tests will be used to assess organism health during the given assay period and the influence of the "clean" water on the organism. The response of the organisms in the control samples must equal or exceed the response limits for each of the bioassays presented in Table 6.

An additional form of "reagent blank" will be used during fish bioaccumulation studies. Preexposure samples of the fish population will be performed to establish a background concentration of contaminants in the test organism. Preexposure fish may have detectable levels of some contaminants, but should be below the levels identified in the exposed fish.

Control charts, with $\pm$ 2 and 3 σ values (the 95 and 99 percent confidence intervals) as warning and action limits, respectively, will be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter.

Table 5. Measurement quality objectives for inorganic and organic chemistry analyses for the ARCS program[a].

Parameter	MDL[b] Sediment (µg/kg)	Tissue (µg/kg)	Elutriate (µg/L)	Water (µg/L)	Accuracy[c]	Frequency	Precision[d]	Frequency
Metals[e]	2000	2000		1	± 20%	1/batch	≤20%	1/batch
except Ag	100	100	1		± 20%	1/batch	≤20%	1/batch
Cd	100	100	1		± 20%	1/batch	≤20%	1/batch
Hg	100	100	0.01		± 20%	1/batch	≤20%	1/batch
Ca				10	± 20%	1/batch	≤20%	1/batch
Mg				1	± 20%	1/batch	≤20%	1/batch
Methylmercury	10	10	0.0001		± 20%	1/batch	≤20%	1/batch
Tributyltin	10	50	0.01		± 20%	1/batch	≤20%	1/batch
PAHs	200	200		2	± 20%	1/batch	≤20%	1/batch
Pesticides	10	4		0.05	± 20%	1/batch	≤20%	1/batch
PCB/congener	0.5	1		0.01	± 20%	1/batch	≤20%	1/batch
PCB/aroclor	20			0.01	± 20%	1/batch	≤20%	1/batch
Dioxins/Furans	0.002	0.002		0.01	± 20%	1/batch	≤20%	1/batch
TOC/DOC	0.03%			1000	± 20%	1/batch	≤20%	1/batch
O&G	10000				± 20%	1/batch	≤20%	1/batch
pH	N/A		N/A	N/A	± 0.1 unit	1/batch	± 0.1 unit	1/batch
Ammonia			360	360	± 20%	1/batch	≤20%	1/batch
AVS	1000				N/A	N/A	≤20%	1/batch
Organohalogens[f]	30 ng				± 20%	1/batch	≤20%	1/batch
Sulfides				10	± 20%	1/batch	≤20%	1/batch
Total S	10000				± 20%	1/batch	≤20%	1/batch
Chlorides				200	± 20%	1/batch	≤20%	1/batch
Alkalinity				1000	± 20%	1/batch	≤20%	1/batch
Hardness[g]				2000	± 20%	1/batch	≤20%	1/batch

Table 5 (cont). MQOs for inorganic and organic chemistry analyses for the ARCS program[a].

Parameter	MDL[b] Sediment (µg/kg)	Tissue (µg/kg)	Elutriate (µg/L)	Water (µg/L)	Accuracy[c]	Frequency	Precision[d]	Frequency
DO				10	± 0.5 mg/L	1/batch	± 0.1 mg/L	1/batch
Conductivity				N/A	± 1 µS/cm	1/batch	± 2 µS/cm	1/batch
Chlorophyll-a					100	± 20%	1/batch	≤20% 1/batch
Total solids		0.001g				N/A	N/A	≤20% 1/batch
Volatile solids		0.002g				N/A	N/A	≤20% 1/batch
TSS				0.001g	N/A	N/A	≤20%	1/batch
PSA[h]	0.001g				windows	1/batch	≤20%	1/batch
SER	0.001g				± 20%	1/batch	≤20%	1/batch
Moisture content		0.001g				N/A	N/A	≤20% 1/batch
Lipid content	0.001g				± 20%	1/batch	≤20%	1/batch

a - MQOs presented do not apply to the measurement of water quality parameters associated with bioassays or fish bioaccumulation studies.

b - MDLs for water include pore water and water column samples. Units presented in subheading are applicable to all parameters unless otherwise noted. If no MDL is presented, then that parameter is not measured in that given matrix. N/A = not applicable.

c - accuracy determined from CRM, SRM, or standard and is measured from the known concentration.

d - precision is calculated as %RSD. It should be noted that LLRS will only be performing duplicate analyses, therefore, the limit will be calculated as a RPD. Precision requirements listed here are for analytical replicates only, field duplicates are required to have a RPD ≤ 30%.

e - metals include Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn. Exceptions are noted where different methodologies are used during the metals quantitation. Ca and Mg are used by SUC-B for determination of water hardness.

f - the MDL for Cl and Br is 30 ng while the MDL for I is 10 ng.

g - hardness determined titrimetrically.

h - PSA = particle-size analysis; a soil sample with acceptance windows per size fraction was provided by LESAT to LLRS for use as an accuracy standard.

Table 6. Measurement quality objectives for bioassays and fish bioaccumulation studies for the ARCS program.

Assay Organism/Community	Endpoint[a]	Response limit (mean)[b]	Reference Toxicant[c]	Precision[d] & Accuracy
Pimephales promelas	Survival	80%	1 CR	60%
	Larval growth	0.25 mg	25% or 1 CR	60%
Daphnia magna	Survival	90%	45%	40%
	Reproduction	60 young	1 CR	40%
Ceriodaphnia dubia	Survival	90%	30%	30%
	Reproduction	15 young	1 CR	40%
Hyalella azteca	Survival	80%	25%	40%
Chironomus riparius	Survival	70%	25%	60%
Chironomus tentans	Survival	70%	25%	60%
Panagrellus redivivus	Survival	80%	25%	40%
	Development	80%	25%	40%
Diporeia sp.	Survival	80%	25%	40%
	Avoidance	80%	25%	40%
	Uptake	80%	25%	40%
Hexagenia limbata	Survival	80%	25%	40%
	Molting Frequency	80%	25%	40%
	Uptake	80%	25%	40%
Selenastrum capricornutum	Growth	200000 @ 96 hrs	30% or 1 CR	85%
	^{14}C uptake	200000 @ 96 hrs	30% or 1 CR	85%
Lemna minor	Growth	50% increase	65% or 1 CR	40%
	Chlorophyll-a	50% increase	65% or 1 CR	40%
Hydrilla verticillata	Chlorophyll-a	80%	20%	60%
	Dehydrogenase Activity	80%	20%	60%
	Shoot Length	80%	20%	60%
	New Growth	80%	20%	60%
Microtox™	Luminescence	N/A	25%	60%

Table 6 (cont.). Measurement quality objectives for bioassays and fish bioaccumulation studies for the ARCS program.

Assay Organism/Community	Endpoint[a]	Response limit (mean)[b]	Reference Toxicant[c]	Precision[d] & Accuracy
Ames Assay (Salmonella)	Revertant Colonies	N/A	25%	N/A
Alkaline phosphatase	Enzyme Activity	20%[e]	25%	80%
Dehydrogenase	Enzyme Activity	20%[e]	25%	80%
β-Galactosidase	Enzyme Activity	20%[e]	25%	80%
β-Glucosidase	Enzyme Activity	20%[e]	25%	80%
Benthic community structure	Abundance of species	N/A	N/A	N/A
Rapid Bioassessment II,III	Community Indices (10)	N/A	N/A	80%

a - for bioassays in which survival is the primary endpoint, MQOs are only presented for the survival endpoint. The additional endpoints, such as avoidance, uptake, development and molting frequency, will be recorded by the PIs.

b - the response limit is presented as the mean of the test replicates in the control or blank sample. For Ceriodaphnia dubia and Daphnia magna the reproduction response limit is the cumulative total of 3 broods. N/A = not applicable.

c - CR = concentration range in the serial dilution assays. The percentages are the maximum %RSD of EC50 and LC50 values allowed among the replicates.

d - precision values presented are the maximum %RSDs allowed among the replicate tests. Accuracy limits presented are the maximum %RSDs compared through time for a given test.

e - background (non-biologically induced response) should by ≤ 20% of the control response.

A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative mean, sample analysis should cease until an explanation is found and the system is brought under control.

For several of the parameters to be measured in the ARCS program, reagent blanks are not applicable due to the nature of the test. For the inorganic parameters of conductivity, DO, pH and TSS, reagent blanks do not exist or are not applicable. Further, reagent blanks are not applicable to the fish tumor and abnormality studies, the determination of benthic community structures, nor community indices to be performed at the NFRC-GL and NFCRC laboratories. Finally, reagent blanks are not applicable to whole sediment toxicity tests.

5.2.4 Reference Materials

Certified reference materials (CRMs) or standard reference materials (SRMs) will be analyzed in the ARCS program to assess the accuracy of measurements being made at the analytical laboratories. These materials are to be purchased by the laboratory from known supply houses such as NIST and the USEPA. If CRMs and SRMs are not available for a given parameter, the laboratory will assess accuracy of the analysis using a standard of known concentration created by the QA officer or QA staff of the analytical laboratory and/or through the use of the ongoing calibration check sample (to be discussed) and/or matrix spike recoveries (to be discussed), where appropriate. The reference materials will be used to control bias and reduce between-batch components of measurement uncertainty. Data for these samples will be evaluated by batch to ensure that the results are within acceptable accuracy limits as defined in this document (section 5.3) and the laboratory's submitted QAPjP. If the reference material does not meet the accuracy window criteria, corrective actions should be taken. These corrective actions can include a recalculation of the data, reanalysis of the samples, and/or reanalysis of the entire sample batch. Notification of the laboratory QA officer should be done immediately upon identification of any problem. It should be noted that reference material are not applicable to the fish tumor and abnormality surveys.

For bioassays and bioaccumulation studies, two forms of reference materials will be used to assess the "accuracy" of organism responses. The first will be to expose the organism to a "reference toxicant" that will have a known and quantifiable response in the organism. The reference toxicants are used to test the organisms sensitivity to waterborne contaminants. The reference toxicants that will be used for these assays will include cadmium chloride, sodium chloride, or copper sulfate for all bioassays and bioaccumulation studies excluding Microtox™. Phenol will be used as the reference toxicant during the Microtox™ testing. The reference toxicants will be used to control bias and assess the within- and between-batch components of the measurement uncertainty.

The second reference material for assessing the "accuracy" of the bioassay and bioaccumulation studies is the use of a reference sediment. The reference sediment is a fine silt

clay-sized mineral soil that has been used extensively in sediment toxicity testing (Adams et al., 1985; ASTM, 1989). The reference sediment, also known as the Florissant soil, will expose the organism to a similar matrix to that of the sediments but without the contaminants being present. The acceptability of the toxicity tests will be assessed by the response (survival or growth) of the control organisms to the reference sediment.

Control charts for the reference materials, with ± 2 and 3 σ values (the 95 and 99 percent confidence intervals) as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the test result should be recalibrated and the samples in that batch may need to be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative mean, sample analysis should cease until an explanation is found and the system is brought under control. For the bioassay and fish bioaccumulation tests, control charts of the effective concentration (EC), lethal concentration (LC), no observable effect level (NOEL) or lowest observable effect level (LOEL) values will be prepared.

5.2.5 Matrix Spikes and Matrix Spike Duplicates

Matrix spike samples will be used to assess the efficiency of the extraction technique and as a form of accuracy testing. Matrix spike analyses are to be reported as the percent spike recovery of the known quantity added to the sample for each analyzed parameter. Selection of the sample to be spiked should be at random from the routine samples to be tested. The concentration of the matrix spike samples must not exceed the linear range of the instrument. If necessary, dilution of the spiked sample is permitted. The MQOs for the matrix spike are that the recoveries for inorganic analyses, including TOC and DOC, must be ± 15% of the known added concentration. For organic analyses, the matrix spike should have recoveries within ± 30% of the known added concentration. Matrix spikes should be analyzed at a rate of 1 per batch. It should be noted that matrix spikes are not applicable to analysis of sulfides, chlorides, alkalinity, hardness (if determined titrimetrically), conductivity, DO, pH nor TSS. Further, matrix spikes are not required during bioassays, fish bioaccumulation testing, nor for the water quality parameter determinations associated with these assays.

For liquid samples, e.g., pore waters and elutriates, one matrix spike sample is to be prepared for each analyte to be tested by spiking an aliquot of a solution with a known quantity of analyte prior to analysis. The spike concentration should be approximately 1 to 1.5 times the expected concentration of the sample. Further, the volume of the added spike should be negligible, i.e., less than or equal to one percent of the sample aliquot volume.

For solid samples, e.g., sediments, one matrix spike will be prepared for each analyte by adding a known weight of material containing the analyte of interest (i.e., for TOC) or a known volume of the analyte with a known quantity of the analyte into the sediment prior to sample extraction or digestion. The spike concentration should be approximately 1 to 1.5 times the expected

concentration of the sample. If a solid phase spike is added, its weight should be considered negligible for the purposes of quantifying the spike recovery.

A matrix spike duplicate will be prepared and analyzed for the treated solids obtained as a result of the testing of remedial technologies by the E/T workgroup. The matrix spike duplicate will be used to check the reproducibility of the remedial technology results and provide an additional confirmation of the extraction technique efficiency. The matrix spike duplicate will be prepared only for the organic contaminants, namely, the PCBs and PAHs, for which the remedial technology is supposedly degrading and/or removing from the sediment. The matrix spike duplicate should be prepared and analyzed on the same sample selected at random for the matrix spike, in the same manner as the matrix spike, and at the same frequency as the matrix spike previously discussed in this section. The acceptance limits for the matrix spike duplicate recoveries are the same as for the matrix spike and the RPD between the matrix spike and matrix spike duplicate should be $\leq$ 30%.

If the MQO criteria established for matrix spike recoveries or matrix spike duplicates are not satisfied, corrective action should be implemented. These corrective actions can include a recalculation of the data, recalculation of the percent recovery, respiking of the sample followed by subsequent requantification, and/or reanalysis of the entire sample batch. Notification of the laboratory QA officer should be done immediately upon identification of any problem.

5.2.6 Surrogate Spikes

Surrogate spike analyses are only applicable to the organic analyses of PCBs, pesticides, PAHs, and dioxins/furans. A surrogate spike is defined as the addition of an organic compound which is similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in the environmental sample (USEPA, 1986). These compounds are spiked into all blanks, standards, samples, and spiked samples prior to extraction. Percent recoveries are calculated for each surrogate compound.

The MQO for the surrogate spike analysis is that the surrogate spike recovery should be ± 30% of the known added concentration. If the criteria established for surrogate spike recoveries are not satisfied, corrective action should be implemented immediately. These corrective actions can include a recalculation of the data, recalculation of the percent recovery, respiking of the sample followed by subsequent requantification, and/or reanalysis of the entire sample batch. Notification of the laboratory QA officer should be done immediately upon identification of any problem.

5.2.7 Ongoing Calibration Check Samples

The ongoing calibration check sample is analyzed to verify the calibration curve prior to, during, and after any routine sample analyses. The concentration of the ongoing calibration check samples should be about mid-calibration range for the given analyte. The MQO for the ongoing calibration check samples is that the measured concentration should be ± 10% of the known concentration. Ongoing calibration check samples should be run at a the beginning, middle, and end of each batch

of inorganic analyses and at the beginning, every 12 samples, and the end for organic analyses. Corrective actions if the ongoing calibration check samples does not meet its MQO can include a recalculation of the data and recalibration of the instrument followed by the reanalysis of the sample batch associated with the "bad" ongoing calibration check sample. Notification of the laboratory QA officer should be done immediately upon identification of any problem.

Control charts for the ongoing calibration samples, with ± 2 and 3 σ values as warning and action limits, respectively, will be required to be created and updated after each day of analysis to control any systematic bias that may be adding to the overall measurement uncertainty for a given parameter. A value outside the control limits is considered unacceptable, hence, the instrument should be recalibrated and the samples in that batch should be reanalyzed. If bias for a given analysis is indicated, i.e., at least seven successive points occurring on one side of the cumulative means, sample analysis should cease until an explanation is found and the system is brought under control.

The ongoing calibration check sample is not applicable to the gravimetric analyses (such as TSS, total solids, etc.). Ongoing calibration check samples are also not applicable to the bioassays, fish bioaccumulation studies, or the water quality parameters to be examined in conjunction with these assays, as well as for the fish tumor and abnormality surveys.

5.3 Description of Measurement Quality Objectives

The following text will describe the DQOs and MQOs as they apply to the sampling and analytical phases of the ARCS program. Implementation of the MQOs during the ARCS program will be described in section 6.

The structure of the MQO table for the physical, inorganic, and organic analyses (Table 5) is as follows:

- Parameter - contaminant being analyzed,
- Reporting units - analytical units in which the laboratory data should be reported,
- MDL - method detection limit expressed in reporting units by media in which the sample is to be analyzed,
- Accuracy - limits of acceptance for CRM, SRM, and other standards and their required frequency of use, and
- Precision - limits of acceptance for analytical replicates and their required frequency of use.

The structure of the MQO table for the bioassays (including benthic community structure determinations) and fish bioaccumulation studies (Table 6) is as follows:

- Assay organism/community - test being performed,
- Endpoint - result being measured or observed,

- Response limit - limits of acceptance for the mean of the replicate samples for the control blanks,
- Reference toxicant - limit of acceptance for organism response to known toxicant, and
- Precision & Accuracy - limit of acceptance for among test replicates and organism response limits to use of the reference sediment.

5.3.1 Field Sampling and Mapping

Sediment sampling includes the physical removal of sediment samples from the core tube, grab sampler, bucket sampler, etc., as well as the characterization of the sediment and the sampling site for the T/C and E/T workgroups. Members of the T/C workgroup will also be collecting fish tissue samples for contaminant level determinations and whole fish for tumor and abnormality classification and quantitation. Members of the RA/M workgroup will be involved in the collection of water column and suspended sediment/particulates, CSOs, and fish samples to support their modeling efforts. In addition to sample collection, the T/C workgroup will also be mapping sediment depths and layering for each of the sampled AOCs. Since the MQOs developed for the laboratory operations are not applicable to the sampling and mapping efforts, specific objectives for sediment and water sampling have been developed to ensure that field operations, e.g., sampling, will be conducted in a consistent manner. The objectives are intended to reduce the errors inherent in collecting sediment data and to provide an estimate of the variability within the sediment.

The goals of the ARCS program sampling programs are to describe and collect sediment, water column, CSO, and fish samples from representative sites. Multiple fish samples will be collected and used to represent the typical population found in the sampled AOC. The field sampling programs produce both qualitative data from sediment characterizations and mapping as well as quantitative data from the analysis for the sediment samples, fish tissue, water, and river flow conditions.

5.3.1.1 Precision and Accuracy

Due to the subjective nature of sediment characterization, values for precision and accuracy cannot be determined. However, attempts to control precision and accuracy will be made by having one person be responsible for performing all of the qualitative sediment characterization for the ARCS program. An additional form of control and assessment of the sediment characterization will be accomplished through the videotaping of each reconnaissance station sample and through various auditing techniques for all stations discussed in a later section. Precise site locations will also be determined using the LORAN-C coordinate system, the global positioning system, and through triangulation observations in the event that a resampling of the site is necessary.

Precision and accuracy MQOs have not been established for the sediment mapping program due to the experimental nature of the program. However, precision can be assessed for the profiling results using readings taken from the tie points in the sampling pattern (see section 4.1.1.3 for more detail). The tie points are those positions at the intersection of different profiling passes which

result in the duplicate readings being taken at the same location. Accuracy will be assessed through comparison between the results obtained from the electronic bottom profiling systems and the results observed in core sample collected at the same locations.

Field sampling precision will be assessed for the reconnaissance stations using the data from the field duplicate samples to estimate the system measurement uncertainty and comparing this uncertainty to that identified in the analytical samples. The field samples are expected to contain the largest amount of confounded error of the QC samples. The MQOs for precision of the chemical and biological (Microtox™ assay) parameters associated with the indicator parameter field duplicate should have an RPD of $\leq$ 30%. These duplicate samples will be collected at a rate of one per day per sampling trip. Duplicate samples will be collected for all major depositional horizons/layers identified in the replicate core sample by the field crew. It should be noted that the MQOs established for field sampling are not intended to control field sampling error but are used to assess this error component and to control within-laboratory error occurring at the analytical laboratory.

5.3.1.2 Representativeness

For the collection of master stations for the T/C workgroup, samples were collected in bulk at locations determined at the consensus of the workgroup. Selection of the sampling sites was based on historical sediment contaminant concentrations, input from local authorities on known contaminant discharges and sources, and a desire to provide some degree of complete geographic coverage of the entire AOC. Further, sampling sites were selected in each AOC that represent a gradient of contaminant concentrations, ranging from stations considered to be relatively uncontaminated to known "hot spots" of high pollutant content, thereby, representing all sediment condition scenarios present within the given AOC. During the actual sample collection of the surficial sediments, the boat will be moved periodically to ensure that only surficial sediments are being collected.

During the collection of the reconnaissance stations for the T/C workgroup, sampling locations will be collected throughout the entire designated AOC with a concentrated effort being made at a known "hot spot". Samples and bottom profiles will be collected to give the best possible geographic coverage of the AOC. The intensive sampling of the "hot spot" will provide detailed information on the contaminant levels and distribution. Additional samples will also be collected at the ten initial master sites so that correlations can be made between the detailed analyses to be performed on the master stations and the indicator parameter analyses that will be performed on the reconnaissance stations.

The basic premise in the collection of samples for the RA/M workgroup during the mini-mass balance/synoptic surveys is to collect information about the river system during several periods of low flow (or quasi-steady state) conditions as well as during at least one high flow event (after a major storm system has passed through the AOC or during the spring snow melt). These events will, hopefully, represent conditions commonly found in the river system.

Representativeness is not a major concern for the field sampling efforts of the E/T workgroup. The primary goal for the E/T workgroup sampling is to collect a bulk sample that is grossly contaminated with a given class or classes of contaminants. The collected samples will, hopefully, contain several representative contamination scenarios that have been identified in the Great Lakes basin.

Both the qualitative and quantitative data collected are intended to be representative of the sediments, fish, or water conditions at each AOC.

5.3.1.3 Completeness

The completeness objective for field sampling is set at 90% for the T/C and RA/M workgroups. Hopefully, 100 percent of the stations/sites can be sampled but inclement weather conditions are expected to hinder or limit (in the case of ice) the sampling program. A completeness of 100% is expected for the E/T workgroup sampling effort.

5.3.1.4 Comparability

Comparability for field sampling will be maintained by having one laboratory (LLRS) collect all the samples (master and reconnaissance station) for the T/C workgroup using USEPA approved methods. Bottom sediment mapping efforts will maintain comparability by having only a single laboratory perform all the profiling for the whole ARCS program. Within the RA/M workgroup, sample collection will also be performed using USEPA approved equipment and methods that are similar, if not identical, between the two AOCs to be characterized, thereby maintaining comparability of the sampling techniques. E/T workgroup sample collection will follow standard USACE dredging practices or practices being utilized at the Sheboygan Harbor or Ashtabula River Superfund sites. For the three ARCS program primary AOCs, the collected bulk sample will be homogenized and distributed to all participating laboratories from ERL-D.

5.3.2 Laboratory Analysis

The analysis phase of the ARCS program measurements allows the most quantitative evaluation of data quality. The following sections will discuss the five basic quality assurance objectives as well as detectability.

5.3.2.1 Detectability

The data users have determined specific levels of instrument detection for the parameters being analyzed. The MDLs for these instrument determined parameters and their appropriate reporting units are listed in Table 5. The MDLs listed in Table 5 are broken down by the media in which the analysis is going to be performed. These media include sediment, fish tissue, elutriates, and water (which includes pore water and water column samples). It should be noted that not all parameters are to be analyzed in all media. MDLs are only presented for those medium in which

analyses are to occur and are known at this time. Method detection limits for the ARCS program are defined as 3 times the standard deviation of the measured concentration of 15 or more blanks or low-level standards whose concentrations are within a factor of 10 of the ARCS required IDL. MDLs should be determined prior to any analysis of routine samples and should be determined for each instrument used for the element(s) or compound(s) quantification.

It should be noted that for the detection limits of organic contaminants associated with the mini-mass balance/synoptic surveys performed by the RA/M workgroup, that the MDLs may have to be lowered in order to obtain 90% or more of the samples having detectable contaminant levels. A lesser number of samples with quantifiable contaminant concentrations could severely restrict the modelers efforts.

5.3.2.2 Precision and Accuracy

The MQOs for precision and accuracy of the physical, inorganic, and organic analyses are provided in Table 5. Accuracy will be assessed through the use of CRMs, SRMs, or other standards and are generally defined as a known value ± an acceptance range. Precision is assessed through the use of replicate samples and generally determining the %RSD or RPD, whichever is appropriate, among the replicates. Exceptions to these generalizations are presented in the tables. It should be noted that precision of the water quality parameters used in conjunction with bioassays and fish bioaccumulation studies is the only quality assurance objective required in the ARCS program, excluding the need for proper initial calibration of the instrument, probe, titrator, etc.

The MQOs for precision and accuracy for the bioassays and fish bioaccumulation studies are presented in Table 6. Accuracy will be assessed through the use of the reference sediment, reference toxicant, and long-term monitoring of the coefficients of variance among reference toxicant use for a given bioassay. Precision will be measured by determining the %RSD among the replicates performed for each of the tests.

5.3.2.3 Representativeness

The integrity of the sediment, water, fish tissue, and elutriate samples is to be maintained during sample analysis activities. Homogenization of the samples prior to shipment to the analytical laboratories as well as a second homogenization of the received sample at the laboratory will help ensure that a uniform stock of sample is available from which aliquot selection for analysis can be made. Homogenization of bulk samples will be performed in cement mixers for a fixed amount of time with homogeneity being determined visually by obtaining a sample with consistent color, texture, and water content throughout the entire sample. At the analytical laboratory, the sample homogenization will be performed via stirring, by hand or mechanically, until visual homogeneity in terms of color, texture, and water content are obtained. Once the sample is deemed to be homogeneous at the analytical laboratory, aliquots will be taken of solid phase samples randomly by the insertion of the sampler (spatula, spoon, knife, etc.) and collecting the sample.

5.3.2.4 Completeness

The completeness objective for all inorganic and organic parameters analyzed is set at 90 percent or better. The completeness objective for the bioassay and fish bioaccumulation studies is set at 80 percent or better. It is possible to attain 100 percent completeness if a sufficient quantity of each sample is available to complete all analyses and reanalyses that may be necessary. Completeness for the fish tumor and abnormality studies is set at 100 percent determination and quantification of the fish collected from the field.

5.3.2.5 Comparability

Analytical data from the ARCS program is expected to be comparable among the laboratories involved through the use of standardized, documented, accepted USEPA methods or their equivalents and through the use of common reporting units. Comparability of the analytical results will also be assessed through the replication of some analytical procedures and bioassays on the "same" sediment sample by different analytical laboratories.

Section 6

Quality Assurance Implementation

6.1 Control of Data Quality

The following subsections describe the methods used to control the quality of data produced during the various data collection phases and to ensure that the MQOs described in section 5 are being met.

6.1.1 Field Sampling and Characterization

Control of data quality in the sampling phase of the ARCS program is primarily a responsibility of the various sampling crews. A field audit (to be discussed in section 6.1.3.3.1) will be performed by the EMSL-LV and LESAT QA staff to help control the quality of the field sampling and characterization program. The following sections will discuss the QA implementation for the field sampling program as they relate to the quality assurance objectives.

6.1.1.1 Precision and Accuracy

In order to ensure the precision of the field sampling and characterization program for the reconnaissance stations, duplicate core samples will be collected and described during each sampling day in each AOC. If marked differences are noted, both cores should be discarded, two new cores should be obtained after slightly moving the boat so that the recoring will not be from the exact same location. A field audit (to be discussed in section 6.1.3.3.1) will also be performed by the EMSL-LV and LESAT QA staff to help control the accuracy and precision of the field sampling and characterization program.

For the RA/M workgroup sampling program, in association with the mini-mass balance/synoptic surveys, a series of "dry" sampling runs will be performed by the sampling crews prior to collection of ARCS program samples to ensure the working conditions of the collection equipment as well as to familiarize the samplers with the proper operation of the equipment and the needs of the ARCS program. Duplicate samples of the river water, particulate, and CSOs will be collected in the field at a rate of one duplicate per sampling day per AOC during the synoptic surveys to help assess the imprecision error component. Further, a field audit will be performed by the EMSL-LV and LESAT QA staff to ensure that the sampling protocols and QC program is being followed as stated in the laboratory submitted QAPjPs.

6.1.1.2 Representativeness

Representativeness of the field sampling and characterization program will be maintained by the collection of samples throughout the entire AOC for the T/C and RA/M workgroups and at the

locations identified by the workgroup members during their initial meetings. During the sampling program, sediments with a wide range in characteristics and contaminant levels will be collected to represent several different contamination scenarios in the Great Lakes basin. For the E/T workgroup, representativeness of the sediments in the AOC is not a major concern in their field sampling program (see section 4.1.3 for more detail). The E/T workgroup sampling crew is only responsible for the collection of bulk samples that have been grossly contaminated (i.e., high contaminant concentrations).

6.1.1.3 Completeness

Sampling protocols specify that the sampling of 90 percent or more of the designated master stations. Reconnaissance station surveys will collect as many samples as is permitted financially per AOC (approximately 200 samples or 60 cores). If a sampling site is inaccessible, the reason for excluding the site must be formally documented by the sampling crew and reported to the workgroup chair, workgroup members, and GLNPO.

6.1.1.4 Comparability

The consistent use of standardized sampling methods and specified protocols for the sampling phase provides field data that are comparable to data collected at all AOCs for all three workgroups. Comparability is further maintained by using a single laboratory to collect all master and reconnaissance stations for the T/C workgroup.

6.1.2 Laboratory Analysis

Laboratories participating in the analysis of samples in the ARCS program were selected primarily on the laboratory's capacity to provide the services required and ability to produce data of known and high quality (i.e., their expertise in the given areas of analysis). At the request of the workgroup chair or GLNPO staff, pre-award audit samples will be created by EMSL-LV and LESAT to provide an examination of the analytical capabilities of a given laboratory. The results of these analyses will be rated according to the pre-award audit scoring evaluation sheets provided in Appendix A. Further discussion of the pre-award audit program is presented in section 6.1.3.

6.1.2.1 Detectability

The analytical laboratories will be required to make repeated determinations of the IDLs prior to sample analysis. The IDLs serve as an estimate of the lowest concentration of an analyte that an instrument can reliably detect. In addition, the laboratories must satisfy the MDLs, outlined previously in Table 5 for physical, inorganic, and organic analyses, in which the acceptance criteria is that the MDLs $\geq$ IDLs. The laboratories are also required to demonstrate with control charts that the analytical system is under control at all times during analysis. If deficiencies are identified, the laboratory QA officer should be notified immediately and prepare a written report to be submitted to the ARCS QA officer, workgroup chair, and GLNPO staff stating the reasons for the failure to

meet the criteria and proposing a new MDL that can be obtained at the laboratory for ARCS QA approval.

6.1.2.2 Precision and Accuracy

Upon the satisfactory completion of the QA requirements by the analytical laboratory, a data package for each AOC is submitted to the ARCS QA officer and GLNPO database manager for evaluation. The data are evaluated and then validated in accordance with the precision and accuracy MQOs for the various QC samples. Precision for each type of assessment sample must meet the objectives outlined previously in the MQO tables of section 5. Reanalysis may be requested for certain parameters or batches on the basis of imprecise or inaccurate results from the assessment samples, if sample holding times have not been exceeded.

6.1.2.3 Representativeness

Upon receipt of each analytical sample from either the field or laboratory responsible for the homogenization and distribution of the collected bulk samples, the PI or sample custodian is required to re-homogenize the sample, where appropriate, to ensure the representativeness of aliquots used during the analyses. All samples not in use are to be stored at 4 ± 2° C or frozen at -20 ± 5° C, whichever is appropriate for the given sample type, in the dark at the analytical laboratory. Temperatures should be monitored daily and recorded in a bound logbook. If the temperature limits are exceeded, documented corrective actions should be taken to maintain the integrity of the stored samples. Notification of the laboratory QA officer should be done immediately upon identification of any problem.

6.1.2.4 Completeness

The completeness objectives for the physical and chemistry analyses has been set at 90 percent while a completeness of 80 percent is acceptable for the bioassay and fish bioaccumulation studies for the ARCS program. A level of 100 percent completeness may be obtained if sufficient sample is available to complete all routine analyses and reanalyses, where necessary. Completeness for the fish tumor and abnormality surveys has been set at 100% for both qualitative and quantitative analyses of the fish collected from the field investigations.

6.1.2.5 Comparability

Comparability will be maintained through the use of standard documented USEPA methodologies for parameter determinations. If a USEPA method is not available, the method selected should be clearly documented by reference, preferably, with some other form of standard methodologies such as ASTM or by providing a written SOP in the submitted QAPjP. Non-USEPA methods should meet with approval from the ARCS QA officer prior to use in the ARCS program. The QA/QC procedures specified for the analytical laboratories allow for the determination of measurement uncertainty so that the results can be compared among laboratories directly through the replication of some test procedures on the "same" samples by different laboratories or indirectly

through the overall assessment of laboratory performance on a given QC sample type (i.e., reagent blank, replicates, etc.) on a parameter and project basis.

6.1.3 ARCS Audit Program

The ARCS audit program can be divided into three primary sections, namely, the production and grading of audit samples, the conducting of performance audits, and the performance of on-site system audits. Each of these portions of the audit program will be discussed in the following sections.

6.1.3.1 Audit Samples

Upon the request of the GLNPO staff, workgroup chairs, or the laboratories, audit samples containing the analytes of interest will be prepared by the QA staff at EMSL-LV and LESAT. Audit samples will be prepared and analyzed in the same manner as routine samples with the appropriate QA/QC measures being applied as specified in this document and the individual laboratory QAPjPs. Results from the analyses will be graded with an 80 percent representing the minimum passing grade. Audit sample scoring evaluation sheets will be provided in Appendix A. The audit sample scoring evaluation system will be designed to be flexible such that when multiple media and/or mixed chemistry classes (i.e., inorganic and organic) are to be performed, no single medium or chemistry class will dominate the grading scheme. For example, if a laboratory is performing metals analyses in water samples as well as PCBs, PAHs, and pesticides quantification in both sediment and water columns, each class of compounds or medium will be equally weighted in the developed grading scheme.

Audit sample types can be divided into two categories, namely, pre-award and routine audit samples. Pre-award audit samples will be used to assess a laboratory's capability to perform the analyses it will be running on the routine samples. Pre-award audit samples may be either single analyte (i.e., conductivity) or analyte group (i.e., PCBs) or may be composite samples containing several classes of compound (i.e., a mixture of PCBs, pesticides, and PAHs in one ampule). Single analyte or analyte group samples will be used to test quantification efficiency while the composite audit samples will check extraction/cleanup efficiencies in addition to the quantification capabilities of the laboratory.

Routine audit samples are similar to the pre-award audit sample but will only be prepared as composited samples, where appropriate. Routine audit samples will undergo extraction, cleanup, and quantification during the analysis of routine sample batches. Grading of the routine audit samples will be based solely upon the accuracy of the results following the criteria established for reference materials in section 5.2.4.

6.1.3.2 Performance Audits

Performance audits for the ARCS program should involve the inspection of the facilities, discussion of methodologies to be used and QA/QC limits that are applicable with the laboratory technician, and preliminary data review to assess the success/failure of the laboratory's QA program. These audits should be performed by the laboratory QA officer or designee. Upon completion of the audit, a written report should be prepared, maintained on file, and submitted to GLNPO, the workgroup chair, and ARCS QA officer. The report should identify any deficiencies noted, the corrective actions undertaken, and the results of the reanalysis, if conducted. Performance audits should be conducted a minimum of once during the ARCS program preferably at the beginning or near the beginning of the analyses so that any problems can be controlled and corrected early in the program.

A series of performance audits will be performed by GLNPO personnel to ensure the proper functioning of the ARCS QA and database management programs established at EMSL-LV and LESAT. These audits will check the progress of the initial establishment QA program, provide overviews of the operational, established ARCS QA program, provide reviews and status of the ARCS program from the QA point of view (i.e., audit sample results, QAPjP preparation, quality of submitted data, etc.), as well as examine and review the QA/QC validation procedures for the submitted databases (to be discussed in section 6) at LESAT. These audits will be performed annually or more frequently as deemed necessary by the GLNPO staff or members of the AIC.

6.1.3.3 System Audits

A major factor in controlling data quality is the independent on-site system audit, which ensures that all of the program participants are adhering to the protocols in a consistent manner. The system audit team will ideally consist of three external scientists, two from the QA staff at EMSL-LV and LESAT and one from the GLNPO. Members of the audit teams will be selected to provide the expertise in the given subject area (i.e., for the major analyses to be performed at the laboratory) and in the field of QA. The on-site field and laboratory audits will be described in the following text.

6.1.3.3.1 Field System Audits

At least one field system audit will be scheduled for the sampling of the reconnaissance stations to be conducted by the LLRS laboratory for the T/C workgroup and during the collection of samples for the mini-mass balance/synoptic survey conducted by the RA/M workgroup. The audit team will observe the coring procedures, data recording, bottom profiling, and location determination as well as sample collection, handling, preservation, and storage techniques for several days within a selected AOC. Informal checks on the characterization of the cores will be made on sediment characteristics such as texture, layer thickness and boundary determinations, color, and odor. These checks will be performed by the audit team and compared to the results obtained from the sampling crew. If discrepancies are noted, discussions will be held immediately to resolve the problem while

the core is still intact. Upon completion of each sampling day, the audit team will discuss any deficiencies that might influence the integrity of the samples with the sampling crew. A final oral summary of the findings and concerns of the audit team will be presented upon completion of the audit with a subsequent written report being submitted to GLNPO, the laboratory, and workgroup chair. Unfortunately due to the relative lateness of the establishment of the formal ARCS QA program, no field system audits will be performed during master station sampling by LLRS for the T/C workgroup nor during the collection of the bulk samples by the USACE for the E/T workgroup.

6.1.3.3.2 Laboratory System Audits

Each analytical laboratory generating data for the ARCS program can expect at least one on-site system audit. The audits will generally consist of a laboratory tour, data review, and discussions about the concerns identified by the audit team during both the laboratory tour and during data review. During the laboratory tour, the following general elements will be examined or performed:

- analytical instrumentation,
- discussions with laboratory technicians to ensure their working knowledge of the program,
- organism culturing facilities and test areas,
- sample preparation and storage areas,
- sample tracking and documentation, and
- SOPs and logbooks.

These audits will preferably performed approximately one-third of the way through the sample analyses. An evaluation report will be prepared for the audit and submitted to GLNPO with copies being sent to the laboratory and appropriate workgroup chair or chairs (if work is to be performed for multiple workgroups). The laboratory may respond to the audit report in a written manner and/or may request an additional audit to show that all the deficiencies have been eliminated. No system audits will be scheduled for laboratories that produce single or limited (< 5 parameters) measurement data.

6.2 Data Validation/Verification

The intent of this section is to give a brief overview of the various mechanisms that may be used in defining and implementing the data validation/verification procedures and the corrective actions that may be taken if the MQOs are not satisfied.

6.2.1 Data Validation

Data validation for the ARCS program will be those analyses or checks that are performed by EMSL-LV and LESAT QA staff on the submitted data to assess the degree of success that a laboratory obtained in meeting the MQOs specified for their project. Data validation will be performed on both the field sampling and characterization data as well as the analytical laboratory

data. Each of these two data types and their validation procedures will be discussed in the following sections.

6.2.1.1 Field Sampling and Characterization Data

Validation of the field sampling and characterization data will be the primary responsibility of the field sampling crews. Field data submitted to EMSL-LV and LESAT should include, at a minimum, the following items:

- sampling dates,
- site location (latitude and longitude),
- sample identification codes/numbers (see section 4.1.1),
- sample preparation, labeling, and shipping,
- number and type of samples collected including field duplicates, trip blanks, etc.,
- sample preservation and storage conditions,
- chain-of-custody/shipping forms, and
- a listing, with explanation, of any departures or problems encountered during sampling that deviate from the written and approved sampling QAPjP.

Data generated for specific analytical parameters in the field, such as pH, dissolved oxygen, light transmissivity, temperature, etc., will undergo the same procedures for data validation as analytical laboratory-generated data that are presented in the next section - section 6.2.1.2.

At EMSL-LV and LESAT, who will act as an intermediate database repository, field data will be examined for consistency, relative accuracy, and completeness of the submitted data and completeness (as defined for the data quality objectives) for the ARCS sampling program. For this discussion, consistency will be defined as the use of the same descriptive terms, reporting units, and station coordinates (i.e., latitude and longitude) throughout the field database. Relative accuracy will be defined as consistency within the reported measurements. For example, the latitudes and longitudes of all sampling sites within a given AOC will be checked to ensure that they are within several minutes of each other and not several degrees. Additional checks on the completeness of the data will be performed by the ODES database management system (to be discussed in section 9) which has been selected as the final database repository. If deficiencies exist in the field data, the laboratories will be contacted and expected to provide the missing or erroneous data.

6.2.1.2 Analytical Laboratory Data

Validation of the analytical laboratory data will be one of the primary responsibilities of the QA staff at EMSL-LV and LESAT. All data will be reviewed for the following items:

- completeness of the submitted dataset in terms of missing data,
- completeness of the submitted data in terms of the completeness quality assurance objective,

- formal submission of the data as indicated by signatures of the PI and laboratory QA officer,
- logbooks, in particular to determine holding time violations,
- raw data including sample weights, extract volumes, dilution or concentration factors, instrument readings (e.g., chromatograms, quantification reports, etc.), and dates of analysis, where appropriate,
- proper frequency of use and successful completion of the established MQOs for QC samples including spikes, replicates, blanks, accuracy standards, reference toxicants, and reference sediments on a dated per batch basis,
- MDLs and their determinative data and dates of determination,
- calibration data on a per instrument per analyte basis with associated calibration plot and successful completion of acceptance criterion,
- QA reports of in-house performance audits and other reports as mandated in the submitted QAPjPs, and
- a discrepancy report indicating at what point during the laboratory operations the formal ARCS QA program was initiated and providing a discussion of the QA program at the laboratory prior to the institution of the ARCS overall QA program.

Data validation will be determined manually by members of the QA staff. If time permits and dependent upon similarity of submitted datasets and QA/QC requirements, a computerized checking system will be developed.

If deficiencies are identified, a data flagging system will be developed at EMSL-LV and LESAT. The data validation flagging system will clearly indicate the type of deficiency (i.e., failure to meet MQOs of QC samples, sample collection problems, etc.), the degree of the deficiency (high or low), and identify miscellaneous problems, such as missing data values. Further, data comparisons will be made among the laboratories that have analyzed the same sediment sample for the parameters. Discrepancy flags for inter-laboratory comparisons will also be developed and applied to the appropriate datasets. A final QA summary for the entire dataset on a per laboratory basis will be created by the ARCS QA officer for incorporation into the final ODES database. The final QA report to be submitted to GLNPO by EMSL-LV and LESAT will contain a complete accounting of all QA/QC violations in the ARCS program.

6.2.2 Data Verification

Data verification will be performed by the ODES system. ODES is designed to perform checks on the appropriateness of submitted data ranges, formats, and codings prior to the uploading of the data into the final repository. If discrepancies are identified, the EMSL-LV and LESAT QA staff will take steps to correct the problem(s) which may include data checking, data entry, or contacting the appropriate laboratory for the missing information. A more complete discussion of the data verification process is presented in section 9.

Section 7

Data Quality Assessment and Reporting

This QAMP has defined the MQOs (see section 5) and described the implementation of the QA program for the ARCS program (see section 6). This section describes the statistical assessment procedures that will be applied to the data and the general assessment of the data quality accomplishments. QA reports to management will also be discussed.

7.1 Statistical Design

7.1.1 Assessment of Detectability

The assessment of detection limits is accomplished on a parameter basis at two different levels, namely, compliance with ARCS specified MDLs and calculation of actual IDLs. The final results will be grouped in tabular form to allow comparisons among the values for any parameter of interest.

7.1.2 Assessment of Precision

A statistical evaluation procedure that has been applied to other USEPA funded large scale programs will be applied to the data in order to assess possible uncertainty stemming from confounded data collection imprecision. An additive model will be used, where an observed value of any characteristic is considered as the sum of the "true" or accepted value plus an error term. This model assumes that data uncertainty is directly related to the error variance (Miah and Moore, 1988).

The error variance is dependent upon the "true" value of the sediment characteristics of interest. Because of the wide range of analyte concentrations for the sediments, it is necessary to separate the concentration range into segments of error variance that serve as estimates of data measurement uncertainty. The ARCS program statistical approach, therefore, requires that the entire analytical concentration range be partitioned into several intervals not necessarily of equal length. An assumption is made that the error variance within each interval is independent of, and changes with, "true" analyte concentration.

Within this framework, the error variance is represented by a step function (Rudin, 1974) where each step value is the error variance for a specific defined interval. A pooled estimate of the error variance is obtained by taking a weighted average of the individual step values, using the corresponding degrees of freedom as the weighting characteristic.

A fundamental difficulty of this approach is assessing the effect of the error variances on the routine sample data. A measure of this effect, delta, is estimated by averaging the step values of

the error standard deviation using the proportion of routine samples in each interval as the weighting characteristic. Since data collection is a multi-phase process and uncertainty accumulates in the data with each progressive phase, the cumulative uncertainty is estimated with the delta values using the QC data.

7.1.3 Assessment of Accuracy

The assessment of accuracy will be based on the ongoing calibration check samples and the use of CRMs, SRMs, or standards for the inorganic and organic analyses while for the bioassays and fish bioaccumulation studies, the assessment of accuracy will rely upon the use of reference toxicants and the reference sediment. The recoveries of matrix and surrogate spikes for the inorganic and organic analyses can also be used in the assessment of accuracy although the error component involved in these samples is confounded by the interactions of the matrix with the spiked element or compound and hence, the extraction efficiency of the analytical methodology. Accuracy for most parameters in the ARCS program is based upon the known concentration of the material plus or minus an acceptance range around that known value.

7.1.4 Assessment of Representativeness

The sampling aspect of representativeness is assessed by comparing the individual site locations and AOC coverage with the locations and expected coverage DQOs.

Representativeness of the measurement quality samples is assessed by comparing the concentration ranges of data from the field duplicates, where collected, to the overall concentration range of the routine sample data. This is accomplished through the application of critical values determined by the Kolmogorov-Smirnov test (Conover, 1980) which assesses the ability of the duplicate samples to track the distribution of the routine sample concentrations.

Representativeness of the homogenization and subsampling procedures at the analytical laboratories may be assessed using precision estimates for the analytical replicate samples.

7.1.5 Assessment of Completeness

Field sampling completeness is assessed by comparing the actual number of stations collected to the number requested during the design phase of the ARCS program. Completeness of the sample preparation and analytical phases are easily calculated using data from the verified database by calculating the number of analyses passing the QA requirements divided by the number of analyses performed at a given laboratory.

7.1.6 Assessment of Comparability

Comparability is perhaps the most difficult of the data quality attributes to assess, primarily because of the many different aspects of comparison that are involved. Following completion of

the ARCS program, a comparison will be made among the laboratories that will focus on method differences, QC sample results, laboratory effects, and other QA features of the program. Summary statistics will be used to collate individual values into pooled groups that enable the data users to discern trends of interest within the overall ARCS program.

7.2 Quality Assurance Reports to Management

The PIs or QA staffs at each participating laboratory are required to produce at least one written report to document their ARCS program QA activities as well as several oral laboratory updates at the all-hands meetings to be planned throughout the duration of the ARCS program. The general contents of these reports are presented in the following sections.

7.2.1 Status Reporting

Communications among the various participants in the ARCS program should be maintained through conference calls, site visits, release of preliminary draft data, and all-hands and workgroup meetings. These activities provide all participants with the current status of operations and allow prompt discussion and resolution of issues related to the research plan, methodologies, or QA implementation.

7.2.2 Formal Reporting

In addition to the laboratory submitted QAPjPs, the PIs and laboratory QA officers will be required to produce a final written summary of the QA activities and results from their laboratory. This report should accompany the submission of the laboratory QA approved dataset. Other periodic QA reports will be submitted to the ARCS QA officer, workgroup chairs, and GLNPO staff as specified in the laboratory's QAPjP.

In addition to this QAMP, the QA staff at EMSL-LV and LESAT will produce a final QA report which will summarize all aspects of the overall ARCS QA program as related to the entries in the final database. The QA staff will also produce a documented sample/data tracking system such that hardcopy and electronic forms of the database can be easily located, identified, and collated for use and distribution by the staff at GLNPO.

Section 8

Quality Assurance/Quality Control of Historical Databases

8.1 Objectives

In order to assess the environmental impacts resulting from the implementation of remedial alternatives, the RA/M workgroup will perform hazard evaluations of exposures to, and impacts resulting from, contact with contaminated sediments and media containing sediment contaminants incurred by all receptors of concern under the "no action" and other remedial alternatives. The hazard evaluation objectives will draw upon the development and integration of predictive tools to describe future hazards and risks. The development and validation of the hazard evaluation models will proceed in two phases. Phase I will focus on developing modeling tools using existing historic information while Phase II will validate and calibrate approaches developed in Phase I using current synoptic information about the areas obtained during the intensive mini-mass balance studies.

To accomplish Phase I modeling goals, historical datasets will be collected from published reports and utilized in the model development process. One concern that has been expressed by the RA/M workgroup is that the "quality" of the chemistry data to be used in the model construction is unknown. Therefore, a QA/QC evaluation scale for the historical data will be developed by EMSL-LV and LESAT.

The following section will address how the QA/QC evaluation scale will be developed and its intended use in the assessment of the historical data. It should be noted that evaluation scales will only be produced for inorganic and organic chemistry analyses. No evaluation scales will be developed for bioassays, fish bioaccumulation studies, benthic community structures, or fish tumor and abnormality studies.

8.2 Evaluation Scale

The initial phase in the creation of the QA/QC evaluation scale will be to perform an extensive literature search to determine all the possible forms of QA/QC samples that might be applied to inorganic and organic chemistry analyses. Upon completion of the literature search, a second list will be generated for those additional QA/QC practices, not identified through the use of QA/QC samples, that can influence or be used to check the quality of the data. This list will include items such as frequency of QA/QC sample use, exceeded sample holding times, and instrument calibration problems.

The various components will be placed into five general categories, namely, accuracy, precision, spike recovery, blanks, and miscellaneous. These five areas encompass the major areas of concern in a good quality assurance program. Each of the components will then receive a ranking as to its perceived importance in the assurance of high quality data. As a general rule,

higher or maximum values will be assigned to the components of the QA/QC evaluation scale that are essential in a good QA/QC program. Lesser values will be credited to various additional samples that may have been used in the QA/QC design of a given laboratory to assess different system error components.

Contaminants will be grouped into broad categories that cover similar types of elements or compounds. These categories will include: acid volatile sulfides, metals, organometals, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, chlorinated pesticides, chlorinated benzenes, chlorinated naphthalenes, chlorinated dioxins and furan congeners, volatile chlorinated compounds, and miscellaneous analyses (such as particle-size analysis and total organic carbon content). A further subdivision of these broad categories will be performed by analytical matrix (e.g., fish tissue, water column, elutriate, sediment, etc.). Additional or different categories may be used depending upon the grouping of the contaminants in the received datasets.

Upon completion of the assignment of the individual variable values, an acceptance level will be determined for each of the five general categories. The acceptance levels will have a two-fold purpose, namely, (1) to provide a basis for determining the acceptability of the overall dataset or parameter group (such as metals, acid volatile sulfides, etc.), and (2) to provide the data user with the potential to evaluate the dataset further if qualifying flags (to be discussed) are present.

Evaluations of the datasets will be presented to the RA/M workgroup members as the point sum by analyte groupings plus any qualifying flags that might be appropriate. Qualifying flags will be associated with each of the point sums. The flags will be used to indicate some form of deficiency in the dataset such as a failure to meet the project's MQOs for the analyzed QA/QC samples, holding time violations, major methodology differences between that of the ARCS program and that used during the actual sample analyses, or any other factor that could adversely affect the quality of the generated data. Further, the flags will indicate the direction of the deficiency identified in the dataset (i.e., above or below the established MQOs of the original project).

It is intended that the final evaluations will not preclude the use of any data in question in the development of the model. Any and all data may be used at the discretion of the data user. These ratings will be simple indicators to inform the data user of the quality of data that is being incorporated into their model's development.

Section 9

Data Management System

9.1 Ocean Data Evaluation System (ODES)

The Ocean Data Evaluation System (ODES) is a mainframe computerized system that is in production at NCC on the IBM 3090 system. ODES was designed to support the decision making processes associated with marine/water monitoring programs. Since ODES was originally designed for saltwater systems, some modification of data fields will need to be made to adapt the system for the fresh water environment analyzed in the ARCS program.

ODES is comprised of three separate components: the ODES database, ODES reporting and graphical tools, and ODES menu system. Through the ODES menu system a user may access information stored in the ODES database and use the ODES tools to produce analytical reports. The ODES database will combine source input information with river, harbor, and bay environmental information including biological data, sediment pollutant data, and water quality as well as physical/chemical and oceanographic data.

At this time, ODES can accommodate many different kinds of environmental data. These categories that are appropriate for the ARCS program including the following:

- Benthic infauna,
- Bioaccumulation,
- Fish pathology,
- Water quality,
- Sediment grain size,
- Sediment pollutants, and
- Bioassays.

During the data review process at LESAT, any missing data file types will be reported to GLNPO. The GLNPO database manager will then make contact with Tetra Tech, Inc., of Bellevue, Washington or American Management Systems, Inc. of Arlington, Virginia, for the creation of new modules or modification of existing modules to allow for the entry of all ARCS data into the final ODES-based data repository.

9.2 Overview of the Databases

There are two types of data collected for the ARCS project, the field sampling data and the analytical laboratory data which includes the QA/QC data. Each type of data has its own requirements and components which will be discussed in the following sections.

9.2.1 Field Sampling Data

The field sampling data is information about the sample and sampling area. Data concerning the sampling area would include the river/bay/harbor sampled, type of station (master or reconnaissance), latitude and longitude of each site, map location and identifiers, meteorological conditions, river stage, flow velocity, and flow direction. Data concerning the sample would contain the following information: sampling equipment used, sample weight/volume collected, sample number, type of sample (sediment, water column, particulate, CSO, etc.), depositional horizon/layer characteristics, such color, texture, and odor, as well as the time and date of collection, agency, and sampling crew identification.

9.2.2 Analytical Laboratory Data

The analytical laboratory data is the physical, chemical, and biological analyses performed on the samples. Data will generally include the type of test, parameter to be analyzed, routine analytical results on each sample, QC results, and calibration information, where appropriate. Data for a particular sample will include the following: sample number, extraction procedure, reporting units, sample dry weight (moisture content), laboratory applied flags, and the associated results from spikes, replicates, accuracy standards, ongoing calibration check samples, control, reagent blanks, reference toxicants, and reference sediments, where applicable.

9.3 Database Processing, Validation, and Verification

All data, after QC checks, will be stored in the ARCS ODES database. The ARCS database will hold all information that is submitted to the ODES system. The database will contain both field and analytical laboratory data. Upon receipt of the data, computer processing will begin at LESAT. It should be noted that data can be received in any computer-readable format from the analytical laboratories. Generally, the processing of received databases will proceed in the following manner:

1) incorporation of received data into SAS,
2) conversion of incorporated data to a SAS shell database,
3) validation of the database,
4) addition of the QA/QC report by LESAT,
5) conversion of SAS dataset to ODES readable database (ASCII format),
6) submission of database for uploading and checking into ODES,
7) verification of the database by checking for validity of format, codes, and data ranges by ODES, and
8) uploading of the verified data into the final mainframe repository.

The ODES system is highly dependant on the use of coded information to represent internal data fields. Three different general classes of codes, excluding header and sample identifier codes, will be used in the ODES system, namely, chemical codes, taxonomic codes, and miscellaneous codes which include data qualifiers (e.g., the data represents the mean, blank corrected, or below

the MDL), bioassay types, material analyzed (sediment, tissue, water), sampling gear type, meteorological conditions, and chemical analysis methods. Use of these codes allows for the rapid, rigorously formatted, systematic entry of data into ODES as well as limiting the required storage space for any given dataset.

Data entered into the ODES format is stored as a series of records that are specifically combined by ODES into a final data file. Each file converted to the ODES format is composed of a series of general record types which are as follows:

- Survey header record which includes report information common to the entire dataset (e.g., investigator's name, survey dates),
- Station header record which includes information about the station where the sample was collected (e.g., location, water depth),
- Sample record which includes information about each samples (e.g., depth of core, gear used to collect sample),
- Station environment record which is used to record information about the environmental conditions at the station where the sample was collected (e.g., temperature),
- Data record which reports information on pollutant concentrations found in each of the samples,
- Header record of QA/QC samples for reporting blanks, spikes, and other QA/QC samples referred to within the dataset,
- Species abundance data record used in benthic community structure determinations to report species abundance counts,
- Biomass data record which reports biomass for each species or higher level taxa group, and
- Bioassay conditions record which includes information on type of bioassay conducted and the physical conditions under which tests were conducted (e.g., photoperiod, static or flow-through conditions).
- Bioassay data record for reporting Microtox™ luminescence results, bioassay survival percentages, number of offspring produced (for reproductive bioassay endpoints), larval abnormalities, dry weight of animal (for growth endpoints of Pimephales promelas), length and growth of roots, fronds, and shoots, enzyme activity, LC50 values, EC50 values, and substrate cover.

The data records also will contain information about specific data and flags. There are separate variables for QC measures, such as spike recoveries and CRMs usage and acceptance ranges. Other variables will specify a series of codes which are used to identify the samples in ODES. These variables include the source code, series code, year, and scan code. The source code is a two character code that will indicate the location of the sampling survey, e.g., BR = Buffalo River. The series code is to help separate different media analyzed from the same sample or sampling site. Series codes will be as follows:

- P = Pore water,
- E = Elutriate,

- W = Water,
- T = Tissue,
- S = Sediment,
- R = Particulates, and
- O = Oil.

Scan codes will be applied to the data to indicate the time or year by quarter or month in which the sampling event occurred.

Each data record has an internal structure that is specific to the file type and level. Data are stored in fields of these records. Each field is designed to accommodate a particular kind of data, and the order of these fields, the spacing between them, and the format of their contents are carefully defined to allow unambiguous and error-free data entry. Each record in the database will represent one chemical analyzed per sample set. It should be noted that not all records are applicable to all analyses (e.g., the species abundance record is not applicable to sediment pollutant data files). The ODES system automatically selects which are appropriate to the type of data being entered into the system.

Verification of the data will take place before the data are added to the final ARCS database. After the data have been converted to the ODES format, the data will be visually checked to insure no errors occurred during the processing of the data. Further, a flagged data file will be created by ODES, reviewed, and appropriate changes made to the database. The ODES system will verify that all codes, ranges of data, and formats are appropriate and allowed in ODES. Upon completion of all the data validation/verification checks, the database will be uploaded onto the mainframe computer system and will thus become available to all investigators and the general public.

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Appendix A

Analytical Laboratory Pre-Award Evaluation Scoring Sheet

This appendix presents an example of the pre-award audit sample evaluation scoring sheet. This particular scoring system has been developed for analyses that will be performed at SUC-B in which numerous parameters in both inorganic and organic classes are to be quantified. The resultant score must be greater than or equal to 80 percent for the laboratory to be allowed to perform analyses on routine samples in the ARCS program.

PRE-AWARD SCORING SHEET FOR ARCS PROJECT

LABORATORY:
LABORATORY DIRECTOR:

Quantitation of Inorganics: _____
Quantitation & Identification of Organics: _____
Quality Control for Inorganics: _____
Quality Control for Organics: _____
Miscellaneous: _____

TOTAL SCORE: _____ (maximum total points = 1388)
PERCENTAGE: _____%

NOTE: A minimum "passing" score is 80%.

Scored by:

_____
Brian A. Schumacher, Ph.D.
ARCS Quality Assurance Officer

PART I. QUANTITATION OF INORGANICS

Parameter	Points	Pts Awarded (Samples) 1	Pts Awarded (Samples) 2	Total Score
Pb (water)	5			
Fe (water)	5			
Cu (water)	5			
Pb (soil)	5			
Fe (soil)	5			
Cu (soil)	5			

Parameter	Points	Pts Awarded (Samples) 1	Total Score
Conductivity	3		
Hardness	3		
Alkalinity	3		

Parameter	Points	Pts Awarded (Samples) 1	Pts Awarded (Samples) 2	Total Score
TOC	5			

PART II. QUANTITATION AND IDENTIFICATION OF ORGANICS

Parameter	Points	Pts Awarded (Samples) 1	Pts Awarded (Samples) 2	Total Score
α-chlordane	5			
γ-chlordane	5			
Dieldrin	5			
DDT (total)	5			
PCB 1016	5			
PCB 1221	5		N/A[a]	
PCB 1248	5	N/A		
PCB identification	10			
(a)anthracene[b]	5			
(b)fluoranthene[b]	5			
(k)fluoranthene[b]	5			
(a)pyrene[b]	5			
chrysene	5			

[a] = N/A = not applicable.
[b] = benzo compounds (i.e. benzo(a)anthracene).

PART III. QUALITY CONTROL FOR INORGANICS

Sample Type	Pts[a]	Points Awarded: Metals[b]	Metals[c]	Cond.	Hard.	Alkal.	TOC	Total Score
Reagent Blanks								
All < IDL	9			N/A[d]				
One or more > IDL	0							
Certified Reference Material								
All CRMs within ± 20%	15							
One or more CRMs out	0							
Matrix Spikes								
All within 100 ± 15% recovery	20			N/A	N/A	N/A		
One out of criteria	10							
Two or more out of criteria	0							
On-Going Calibration Check								
All within 10%	30							
One or more outside 10% limit	0							
Precision of Replicates								
All %RSD ≤ 20%	15							
One %RSD ≥ 20%	8							
Two or more %RSDs ≥ 20%	0							
Instrument Detection Limits								
All IDLs < ARCS IDL	30							
One IDL > ARCS IDL	15		N/A					
Two or more out of criteria	0							
SUBTOTALS								

[a] - potential points awarded per category.
[b] - metals in water.
[c] - metals in soils used to represent particulates.
[d] - N/A = not applicable.

PART IV. QUALITY CONTROL FOR ORGANICS

WATER SAMPLES

Sample Type	Points*	Points Awarded Pest.	PCBs	PAHs	Total Score
Reagent Blanks					
All < IDL	16				
One or more > IDL	0				
Certified Reference Material					
All CRMs within ± 20%	22				
One or more CRMs out	0				
Matrix Spikes					
All within 100 ± 30% recovery	27				
One out of criteria	17				
Two or more out of criteria	0				
Surrogate Spikes					
All within 100 ± 30% recovery	27				
One out of criteria	17				
Two or more out of criteria	0				
On-Going Calibration Check					
All within 10%	37				
One or more outside 10%	0				
Precision of Replicates					
All %RSD ≤ 20%	22				
One %RSD ≥ 20%	15				
Two or more %RSDs ≥ 20%	0				
Instrument Detection Limits					
Determination and Level	37				
Improper or too high	0				
SUBTOTALS					

* - potential points awarded per category.

PART V. MISCELLANEOUS

This section is for miscellaneous checks such as frequency of use of QC samples, concentration levels in spikes, adherence to protocols, proper reporting units, etc. Individual comments will be listed in this section as they pertain to a given deficiency. All points will be negative in this section.

Pts.	Reasons

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