ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM

EMAP-ESTUARIES VIRGINIAN PROVINCE

1993 QUALITY ASSURANCE PROJECT PLAN

by

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QUALITY ASSURANCE PROJECT PLAN APPROVAL

This quality assurance project plan was developed to assure that all environmental data generated for the Estuaries Resource Group of the Environmental Monitoring and Assessment Program (EMAP) are scientifically valid and of acceptable quality to achieve the program's objectives. The signatures of key technical and management personnel indicate approval or concurrence with the procedures specified in this plan. These approvals and concurrences also represent a commitment to disseminate the plan and the philosophy of total quality to all project participants.

_____ Date

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PREFACE

This document outlines the integrated quality assurance plan for the Environmental Monitoring and Assessment Program, Estuaries Resource Group's Monitoring in the Virginian Province. The quality assurance plan is prepared following the general guidelines and specifications provided by the Quality Assurance Management Staff of the U.S. Environmental Protection Agency Office of Research and Development and the guidelines provided in the draft EMAP Quality Assurance Management Plan.

The primary objective of this Quality Assurance Project Plan (QAPjP) is to maximize the probability that environmental data collected by the EMAP-Estuaries program will meet or exceed the objectives established for data quality. The QAPjP presents a systematic approach that will be implemented within each major data acquisition and data management component of the program. Basic requirements specified in the QAPjP are designed to: (1) ensure that collection and measurement procedures are standardized among all participants; (2) monitor the performance of the various measurement systems being used in the program to maintain statistical control and to provide rapid feedback so that corrective measures can be taken before data quality is compromised; (3) assess the performance of these measurement systems and their components periodically; and, (4) verify that reported data are sufficiently complete, comparable, representative, unbiased, and precise so as to be suitable for their intended use. These activities will provide data users with information regarding the degree of uncertainty associated with the various components of the EMAP-Estuaries data base.

This QAPjP has been submitted in partial fulfillment of Contract Number 68-C1-0005 to Science Applications International Corporation under the sponsorship of the U.S. Environmental Protection Agency. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

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SECTION 1

INTRODUCTION

1.1 OVERVIEW OF EMAP

The U.S. Environmental Protection Agency (EPA), in cooperation with other Federal agencies and state organizations, is conducting research to develop a design for the Environmental Monitoring and Assessment Program (EMAP) to monitor indicators of the condition of the Nation's ecological resources. Specifically, EMAP is intended to respond to the growing demand for information characterizing the condition of our environment and the type and location of changes in our environment. Simultaneous monitoring of pollutants and environmental indicators will allow for the identification of the potential causes of adverse changes. When EMAP has been fully implemented, it will address the following objectives:

- Estimate the current status, trends, and changes in the selected indicators of the condition of the Nation's ecological resources on a regional scale with known confidence.
- Estimate the geographic coverage and extent of the Nation's ecological resources with known confidence.
- Seek associations between selected indicators of natural and anthropogenic stresses and indicators of the condition of ecological resources.
- Provide annual statistical summaries and periodic assessments of the Nation's ecological resources.

1.2 THE ESTUARIES COMPONENT OF EMAP

The Estuaries component of EMAP (EMAP-E) will monitor the status and trends in environmental quality of the estuarine waters of the United States. The EMAP-E Program has set four major objectives:

- Provide a quantitative assessment of the regional extent of coastal environmental problems by measuring pollution exposure and ecological condition.

- Measure changes in the regional extent of environmental problems for the nation's estuarine and coastal ecosystems.

- Identify and evaluate associations between the ecological condition of the nation's estuarine and coastal ecosystems and pollutant exposure, as well as other factors known to affect ecological condition (*e.g.*, climatic conditions, land use patterns).

- Assess the effectiveness of pollution control actions and environmental policies on a regional scale (*i.e.*, large estuaries like Chesapeake Bay, major coastal regions like the mid-Atlantic and Gulf Coasts, large inland bodies of water like the Great Lakes) and nationally.

The EMAP-E program will complement and may eventually merge with the National Oceanic and Atmospheric Administration's (NOAA) existing National Status and Trends Program for Marine Environmental Quality to produce a single, cooperative estuarine monitoring program. To more efficiently manage estuarine activities, the EMAP-E Program has been further divided to study the Great Lakes, the offshore (shelf) environment, and the Nation's estuaries, bays, tidal rivers, and sounds.

Complete descriptions of the EMAP-E monitoring approach and rationale, sampling design, indicator strategy, logistics, and data assessment plan are provided in the Near Coastal Program Plan for 1990: Estuaries (Holland 1990). The strategy for implementation of the EMAP-E project is a regional, phased approach which started with the 1990 Demonstration Project in the Virginian Province. This biogeographical province covers an area from Cape Cod, Massachusetts to Cape Henry, Virginia (Holland et al. 1990). In 1991, monitoring continued in the Virginian Province and began in the Louisianian Province (Gulf of Mexico from near Tampa Bay, Florida to the Texas-Mexico border at the Rio Grande). Additional provinces will be added in future years (e.g., the Carolinian Province in 1994), eventually resulting in full national implementation of EMAP-Estuaries. This document is the Quality Assurance Project Plan for EMAP-Estuaries 1993 monitoring in the Virginian Province.

1.3 QUALITY ASSURANCE PROGRAM WITHIN EMAP

The overall QA and management policies, organization, objectives, and functional responsibilities associated with the EMAP program are documented in a Quality Assurance Management Plan (Kirkland, in preparation). The Quality Assurance Management Plan presents the guidelines and minimum requirements for QA programs developed and implemented by each resource group within EMAP.

1.4 QUALITY ASSURANCE PROGRAM FOR EMAP-ESTUARIES

The Estuaries Resource Group, as a component of EMAP, must conform with all requirements specified in the approved EMAP Quality Assurance Management Plan and also will participate in the EPA mandatory QA program (Stanley and Verner 1983). As part of this program, every environmental monitoring and measurement project is required to have a written and approved quality assurance project plan (QAPjP). The QAPjP for EMAP-E monitoring in the Virginian Province (this document) describes the quality assurance and quality control activities and measures that will be implemented to ensure that the data will meet all quality criteria established for the project. All project personnel must be familiar with the policies, procedures, and objectives outlined in this quality assurance plan to assure proper interactions among the various data acquisition and management components of the project. This document will be revised, as appropriate, as changes are made to the existing QA program, and as additional data acquisition activities are implemented.

EPA guidance (Stanley and Verner, 1983) states that the 15 items shown in Table 1-1 should be addressed in the QA Project Plan. Some of these items are extensively addressed in other documents for this project and therefore are only summarized or referenced in this document.

TABLE 1-1. Sections in this report that address the 15 subjects required in a Quality Assurance Project Plan.

Quality Assurance Subject	This Report
Title page	Title page
Table of contents	Table of contents
Project description	Section 1
Project organization and responsibility	Section 2
QA objectives	Section 4
Sampling procedures	Section 3, 5-10
Sample custody	Section 3, 5-10
Calibration procedures	Section 3, 5-10
Analytical procedures	Section 3, 5-10
Data reduction, validation, and reporting	Section 3, 5-11
Internal QC checks	Section 3, 5-10
Performance and system audits	Section 3
Preventive maintenance	Section 3, 5-10
Corrective action	Section 3, 5-10
QA reports to management	Section 12

SECTION 2

PROJECT ORGANIZATION

2.1 MANAGEMENT STRUCTURE

For the EMAP-Estuaries monitoring in the Virginian Province, expertise in specific research and monitoring areas will be provided by several EPA laboratories and their contracting organizations. The Environmental Research Laboratory in Narragansett, Rhode Island (ERL-N) has been designated as the principal laboratory for EMAP-E monitoring in the Virginian Province, and therefore will provide direction and support for all activities. Technical support is provided to ERL-N through contracts with the following organizations: Science Applications International Corporation (SAIC), Versar Incorporated, and R.O.W. Sciences Incorporated. Additional technical support will be provided through a cooperative agreement with a consortium of universities led by the University of Rhode Island. The Environmental Monitoring Systems Laboratory in Cincinnati, Ohio (EMSL-CIN) will be responsible for analyzing chemical contaminants in sediment samples. The Environmental Research Laboratory in Gulf Breeze, Florida (ERL-GB) has been designated as the principal laboratory for the statistical design of the Estuarine monitoring effort. Figure 2-1 illustrates the management structure for the EMAP-E 1993 Virginian Province monitoring. All key personnel involved in the 1993 Virginian Province monitoring are listed in Table 2-1.

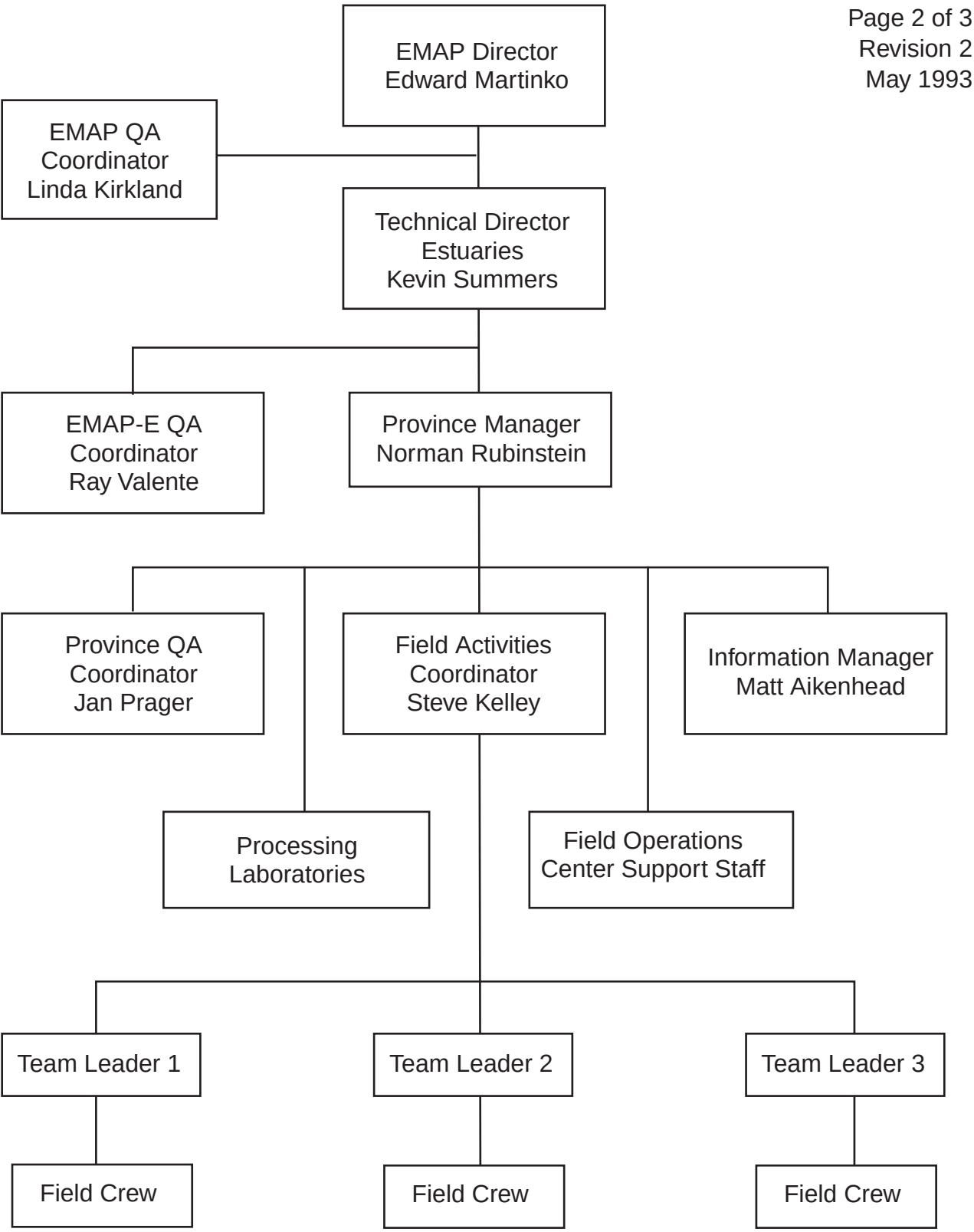

Figure 2-1. Management structure for the 1993 EMAP-E Virginian Province monitoring.

TABLE 2-1. List of key personnel, affiliations, and responsibilities for the EMAP-Estuaries 1993 Virginian Province monitoring.

NAME	AFFILIATION	RESPONSIBILITY
E. Martinko	U.S. EPA-DC	EMAP Director
J. Paul	U.S. EPA-Narragansett	EMAP Associate Director
K. Summers	U.S. EPA-Gulf Breeze	EMAP-E Technical Director
R. Latimer	U.S. EPA-Narragansett	Deputy Technical Director
N. Rubinstein	U.S. EPA-Narragansett	Virginian Province Manager
D. Keith	U.S. EPA-Narragansett	Field Coordinator
D. Heggam	U.S. EPA-Las Vegas	EMAP Logistics Coordinator
D. Reifsteck	SAIC	Logistics/Training Coordinator
S. Kelley	URI/Consortium	Field Activities Coordinator
L. Kirkland	U.S. EPA-DC	EMAP QA Coordinator
J. Prager	U.S. EPA-Narragansett	Virginian Province QA Officer
R. Valente	SAIC	EMAP-E QA Coordinator
C. Strobel	SAIC	Virginian Province QA Technical Support
A. Cantillo	NOAA	NOAA QA Liaison
M. Aikenhead	R.O.W. Sciences, Inc.	Virginian Province Information Manager
H. Buffum	R.O.W. Sciences, Inc.	Virginian Province Database Manager
E. Petrocelli	R.O.W. Sciences, Inc.	Virginian Province Data Librarian
N. Malof	U.S. EPA-Cincinnati	Contaminant Analyses-Sediments
J. Scott	SAIC	Sediment Toxicity Testing
G. Gardner	U.S. EPA-Narragansett	Fish Pathology/Histopathology
G. Thursby	SAIC	Sediment Physical Analyses
J. Frithsen	Versar, Inc.	Benthic Analyses

SECTION 3

GENERAL REQUIREMENTS FOR FIELD AND LABORATORY OPERATIONS

3.1 FIELD OPERATIONS

All field operations conducted by the EMAP-Estuaries Resource Group are planned and implemented according to a logistics plan that is prepared and approved following guidelines established for EMAP (Baker and Merritt 1990). Elements of the logistic plan are presented in Table 3-1, and address major areas of project implementation, including project management, site access and scheduling, safety and waste disposal, procurement and inventory control, training and data collection, and the assessment of the operation upon completion.

TABLE 3-1. Required Elements of EMAP Logistics Plans (from Baker and Merritt 1990).

Logistics Plan Area	Required Elements
Project Management	Overview of Logistic Activities Staffing and Personnel Requirements Communications
Access and Scheduling	Sampling Schedule Site Access Reconnaissance
Safety	Safety Plan Waste Disposal Plan
Procurement and Inventory Control	Equipment, Supplies, and Services Procurement, Methods and Scheduling
Training and Data Collection	Training Program Field and Mobile Laboratory Operations Quality Assurance Information Management
Assessment of Operations	Logistics Review and Recommendations

3.1.1 Training Program

Proper training of field personnel represents a critical aspect of quality control. Field technicians are trained to conduct a wide variety of activities using standardized protocols to ensure comparability in data collection among crews and across regions. Each crew consists of a boat captain, chief scientist, and a minimum of one technician. Minimum qualifications for chief scientists should include an M.S. degree in biological/ecological sciences and three years of experience in field data collection activities, or a B.S. degree and five years experience. The remaining crew members generally are required to hold B.S. degrees and, preferably, at least one year's experience. The captain must be an experienced boat handler, preferably holding a captain's license.

Upon completion of an intensive training session, each chief scientist must pass a practical examination. This examination is useful for assessing the effectiveness of the training session and serves to point out specific areas where further training is warranted. Following the preliminary chief scientist training session, both chief scientists and their crew members must participate in a second intensive training program. Both classroom and "hands-on" training will be coordinated by EMAP-VP Field Operations Center staff members having extensive experience instructing field technicians in routine sampling operations (*e.g.*, collection techniques, small boat handling, etc.). The expertise of the on-site EMAP staff will be supplemented by local experts in such specialized areas as fish pathology, fish identification, field computer/navigation system use, boat handling and water safety, and first aid (including cardiopulmonary resuscitation (CPR) training).

All the sampling equipment (*e.g.*, boats, instruments, grabs, nets, computers, etc.) will be used extensively during the "hands-on" training sessions, and by the end of the course, all crews members must demonstrate proficiency in all the required sampling activities. Upon completion of the formal crew training session, both a written and practical examination will be administered to all personnel. At this time all crews must be satisfactorily checked out in all pertinent areas.

All aspects of field operations are detailed in the Field Operations and Safety Manual (Reifsteck *et al*. 1993), which will be distributed to all trainees prior to the training period. The manual includes a checklist of all equipment, instructions on equipment use, and detailed written descriptions of sample collection procedures. In addition, the

manual includes flow charts and a schedule of activities to be conducted at each sampling location, along with a list of potential hazards associated with each sampling site.

In addition to the formal classroom training and practical examinations, all crews will be evaluated on their field performance during "dry runs" conducted just prior to the actual sampling period. Each crew will be visited during these dry runs by either the Quality Assurance Coordinator (QAC) or the Field Coordinator. Crews may also be evaluated by other personnel at the Field Operations Center for their performance on specific activities, such as data entry, communications and shipping procedures. If any deficiencies within a crew are noted during this final "certification", they must be remedied prior to field sampling. This can be accomplished by additional training or by changing the crew composition. It is the responsibility of the QA Coordinator to develop certification and audit "checklists" and maintain copies of all training examinations, certification results and audit reports in a central file.

3.1.2 Field Quality Control and Audits

Quality control of measurements made during the actual field sampling period is accomplished through the use of a variety of QC sample types and procedures, as described in later sections of this document. In addition, at least once during each field season a QA audit of each field crew will be performed by either the QAC, or his designee, to ensure compliance with prescribed protocols. A checklist has been developed to provide comparability and consistency in this process. Field crews must be retrained whenever discrepancies are noted.

3.1.3 Navigation

Because of the complexity of the navigation equipment and computer system being used aboard the Virginian Province boats, the most important aspect of quality assurance is thorough training of field personnel. Because of the potential to have interferences in the signals (e.g., satellite or Loran) received by the navigation instruments, it is especially important for the chief scientist to evaluate the quality of all inputs and decide which are most appropriate at each station. Once this is decided, proper calibration of the boat's on-board computer navigation system is critical. Calibration information is recorded automatically by the boat computer and must also be recorded in writing in a separate navigation log. Acceptable procedures are discussed in the Field Operations and Safety Manual (Reifsteck *et al.* 1993).

Station location information is logged automatically in the onboard computer through the SAIC Environmental Data Acquisition System (EDAS), which records navigation data through the interface of the Northstar 800X LORAN and Raytheon RAYSTAR 920 Global Positioning System (GPS) units. The EDAS utilizes a Kalman filter which allows navigation through either, or both, of the available positioning systems: GPS and calibrated LORAN-C. The station location, LORAN-C calibration factors, and a series of waypoints can be saved in the EDAS log files for each station. The computer navigation system must be used whenever a station fix is being recorded. Uncalibrated LORAN can result in errors of up to 500 m, and, due to Department of Defense degradation of GPS signals, this system cannot be relied upon for accuracies less than 100 m. Therefore, calibration of the system is essential, and field crews must maintain a separate bound navigation log book to record all LORAN-C calibration information. In addition, crews must record radar ranges and hand-held compass bearings for each sampling station on station location information log sheets, which are later sent to the Field Operations Center for review and permanent storage. Basic navigation, as well as the completeness and accuracy of navigation logs, will be checked during QA audits or visits by senior Program personnel.

As position data are received at the FOC, automatic range checks will be performed on station coordinates (i.e., latitude/longitude). The reported station location will be compared to the expected coordinates and flagged for further investigation if the positions differ by more than one-half mile. If discrepancies are found, original data sheets will be reviewed and/or the chief scientist will be contacted to provide an explanation.

3.2 LABORATORY OPERATIONS

This section addresses only general laboratory operations, while the sections on each indicator present specific QA/QC requirements and procedures associated with the processing of specific samples. All laboratories providing analytical support for chemical or biological analyses must have the appropriate facilities to store and prepare samples, and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. Laboratories are expected to conduct operations using good laboratory practices, including:

- A program of scheduled maintenance of analytical balances, microscopes, laboratory equipment and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (ASTM Class 3, NIST Class S-1, or equivalents).
- Checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons are ± 2 percent of the previous value.
- Recording all analytical data in bound logbooks in ink.
- Daily monitoring and documenting the temperatures of cold storage areas and freezer units.
- Verifying the efficiency of fume hoods.
- Having a source of reagent water meeting American Society of Testing and Materials (ASTM) Type I specifications (ASTM 1984) available in sufficient quantity to support analytical operations. The conductivity of the reagent water should not exceed 1 μS/cm at 25∘ C.
- Labeling all containers used in the laboratory with date prepared, contents, and initials of the individual who prepared the contents.
- Dating and storing all chemicals safely upon receipt. Chemical are disposed of properly when the expiration date has expired.
- Using a laboratory information management system to track the location and status of any sample received for analysis.

Laboratories should be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, control charts and summary data of internal QA/QC checks, and results from certified reference material analyses. Laboratories must also be able to provide analytical data and associated QA/QC information in a format and time frame specified by the Virginian Province Manager and/or Information Manager.

3.2.1 Laboratory Personnel, Training and Safety

Each laboratory providing analytical support to EMAP-E should designate an on-site QA coordinator. This individual will serve as the point of contact for the EMAP-E QA staff in identifying and resolving issues related to data quality. To ensure that the samples are analyzed in a consistent manner throughout the duration of the project, key laboratory personnel should participate in an orientation session conducted during an initial site visit or via

communication with EMAP-E QA staff. The purpose of the orientation session is to familiarize key laboratory personnel with the QA program. Laboratories may be required to demonstrate acceptable performance before analysis of samples can proceed, as described for each indicator in subsequent sections. Laboratory operations will be evaluated on a continuous basis through technical systems audits, performance evaluation studies, and by participation in interlaboratory round-robin programs.

Personnel in any laboratory performing EMAP analyses should be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the laboratory manager and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. The laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA), or equivalent state or local regulations. The safety manual should be readily available to laboratory personnel. Proper procedures for safe storage, handling and disposal of chemicals should be followed at all times; each chemical should be treated as a potential health hazard and good laboratory practices should be implemented accordingly.

3.2.2 Quality Assurance Documentation

All laboratories must have the latest revisions of the EMAP-E Virginian Province QA Project Plan (this document) and Laboratory Methods Manual (U.S. EPA 1992, in revision). In addition, the following documents and information must be current, and they must be available to all laboratory personnel participating in the processing of EMAP-E samples:

- Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory including personnel responsibilities, laboratory acceptance criteria for release of data, and procedures for determining the acceptability of results.
- Laboratory Standard Operating Procedures (SOPs) - Detailed instructions for performing routine laboratory procedures. In contrast to the Laboratory Methods Manual, SOPs offer step-by-step instructions describing exactly how the method is implemented in the laboratory, specific for the particular equipment or instruments on hand.
- Instrument performance study information - Information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information usually is recorded in logbooks or laboratory notebooks.
- Control charts - Control charts must be developed and maintained throughout the project for all appropriate analyses and measurements (see section 3.2.5).

3.2.3 Analytical Procedures

Complete and detailed procedures for processing and analysis of samples in the field and laboratory are provided in the Virginian Province Field Operations and Safety Manual (Reifsteck *et al*. 1992) and the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision) respectively, and will not be repeated here.

3.2.4 Laboratory Performance Audits

Initially, a QA assistance and performance audit will be performed by EMAP-E QA staff to determine if each laboratory effort is in compliance with the procedures outlined in the Methods Manual and QA Project Plan and to assist the laboratory where needed. Additionally, technical systems audits may be conducted by a team composed of the QA Coordinator and his/her technical assistants. Reviews may be conducted at any time during the scope of the study, but are not required every year. Furthermore, laboratory performance will be assessed on a continous basis through the use of internal and external performance evaluation (PE) samples and laboratory intercomparison studies (round robins).

3.2.5 Preparation and Use of Control Charts

Control charts are a graphical tool to demonstrate and monitor statistical control of a measurement process. A control chart basically is a sequential plot of some sample attribute (measured value or statistic). The type of control chart used primarily by laboratory analysts is a "property" chart of individual measurements (termed an X chart).

An example of an X chart is presented in Figure 3-1. Measured values are plotted in their sequence of measurement. Three sets of limits are superimposed on the chart: 1.) the "central line" is the mean value calculated from at least 7 initial measurements and represents an estimate of the true value of the sample being measured, 2.) upper and lower "warning limits" representing the 95 percent confidence limits around the mean value, within which most (95 percent) of the measured values should lie when the measurement process is in a state of statistical control, and 3.) upper and lower "control limits" representing the 99 percent confidence limits around the mean, within which nearly all (99 percent) of the measured values should lie when the measurement process is in a state of statistical control.

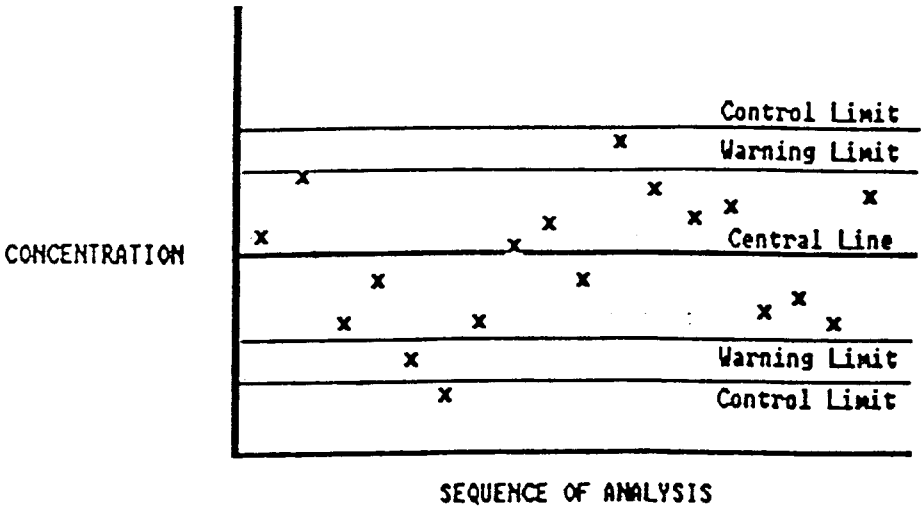

Figure 1-1. Example of a property type of control chart.

Figure 1-1. Example of a property type of control chart.

Control charts should be updated by laboratory personnel as soon as a control sample measurement is completed. Based on the result of an individual control sample measurement, the following course of action should be taken (Taylor 1987):

- If the measured value of the control sample is within the warning limits, all routine sample data since the last acceptable control sample measurement are accepted, and routine sample analyses are continued.

- If the measured value of the control sample is outside of the control limits, the analysis is assumed to no longer be in a state of statistical control. All routine sample data analyzed since the last acceptable control sample measurement are suspect. Routine sample analyses are suspended until corrective action is taken. After corrective action, statistical control must be reestablished and demonstrated before sample analyses continue. The reestablishment of statistical control is demonstrated by the results of three consecutive sets of control sample measurements that are in control (Taylor 1987). Once statistical control has been demonstrated, all routine samples since the last acceptable control sample measurement are reanalyzed.

- If the measured value of a control sample is outside the warning limits, but within the control limits, a second control sample is analyzed. If the second control sample measurement is within the warning limits, the analysis is assumed to be in a state of statistical control, and all routine sample data since the last acceptable control sample measurement are accepted, and routine sample analyses are continued. If the second sample measurement is outside the warning limits, it is assumed the analysis is no longer in a state of statistical control. All routine sample data analyzed since the last acceptable control sample measurement are suspect. Routine sample analyses are suspended until corrective action is taken. After corrective action, statistical control must be reestablished and demonstrated before sample analyses continue. The reestablishment of statistical control is demonstrated by the results of three consecutive sets of control sample measurements that are in control (Taylor 1987). Once statistical control has been demonstrated, all routine samples since the last acceptable control sample measurement are reanalyzed.

Taylor (1987) also provides additional criteria for evaluating control chart data to determine if a measurement system is no longer in a state of statistical control. For X charts, these criteria include:

- Four successive points outside a range equal to plus or minus one-half the warning limits.

- Seven successive points on one side of the central line, even if all are within the warning limits.

- More than 5 percent of the points outside the warning limits.

Central line, warning limits, and control limits will be evaluated periodically by either the on-site QA coordinator or the EMAP-E QA staff. Central lines, warning limits, and control limits for each analyte and sample type will be redefined based on the results of quality control and quality assessment sample measurements. Current control charts must be available for review during technical systems audits. Copies of charts will be furnished to the Province Manager or Province QA staff upon request. Such charts should contain both the points and their associated values.

SECTION 4

ASSESSMENT OF DATA QUALITY

4.1 DATA QUALITY OBJECTIVES

The EMAP-E program is measuring a defined set of parameters that are considered to be reliable indicators of estuarine environmental condition. The measured parameters have been categorized as either biotic condition, abiotic condition, or habitat indicators (Table 4-1) in accordance with the general EMAP indicator development process described by Olsen (1992). More detailed descriptions of EMAP-E's indicator strategy are presented in the Near Coastal Program Plan for Estuaries (Holland 1990).

TABLE 4-1. EMAP-E Virginian Province indicators by major category.

Category	Indicator
Biotic Condition	Benthic species composition and biomass
	Fish community composition
	Contaminant concentrations in fish flesh
	Gross pathology of fish
	Histopathology of fish
Abiotic Condition	Sediment contaminant concentrations
	Sediment toxicity
	Dissolved oxygen concentration
	Marine debris
	Water clarity
Habitat	Salinity
	Temperature
	Depth
	Grain size
	pH

It is the policy of the U. S. EPA that all environmental data collection activities be planned and implemented through the development of data quality objectives (DQOs). Data quality objectives are statements that describe in precise quantitative terms the level of uncertainty that can be associated with environmental data without comprising their intended use. Data quality objectives provide criteria that can be used to design a sampling stategy while balancing the cost and/or resource constraints typically imposed upon a program.

The EMAP is unique in its stated objective of determining ecosystem condition at regional scales using a probability-based sampling design. The relative novelty of this design, coupled with the vast geographic expanse and inherent complexity of the natural systems being monitored, have made the task of developing DQOs a challenging endeavor. Typically, DQOs are specified by potential users of the data. Because EMAP Resource Groups are developing new indicators and employing them in new uses (e.g., regional status and trends estimates), potential users of the data have found it difficult to develop the necessary decision and uncertainty criteria which are basic to the DQO process. In the absence of specific decision criteria established by potential data users, the program has established a set of target DQOs, based primarily on professional judgement, which are intended to provide a starting point for a long-term, iterative DQO process. Consequently, these preliminary DQOs do not necessarily constitute definitive rules for accepting or rejecting results, but rather provide guidelines for continued improvement. Several iterations of the DQO process may be required as EMAP scientists define their capabilities and data users define their needs.

EMAP has established target DQOs for both status and trends estimates. The target DQO for estimates of current status in indicators of condition for EMAP is as follows:

"For each indicator of condition and resource class, on a regional scale, estimate the proportion of the resource in degraded condition within 10% (absolute) with 90% confidence based on four years of sampling."

The target DQO for trends in indicators of condition for EMAP is as follows:

"Over a decade, for each indicator of condition and resource class, on a regional scale, detect, at a minimum, a linear trend of 2% (absolute) per year (i.e., a 20% change for a decade), in the percent of the resource class in degraded condition. The test for trend will have a maximum significance level of alpha = 0.2 and a minimum power of 0.7 (i.e., beta = 0.3)."

It is important to note that the target DQOs which have been established are related to the ability of the present sampling design to characterize status or discern trends within a specified level of statistical confidence. The EMAP-E Resource Group will not be able to begin a realistic assessment of whether it can meet the target DQOs until 1994, when the first four-year sampling cycle will be completed in the Virginian Province. During the first four years of sampling, however, EMAP-E has been actively laying the groundwork for this assessment by gathering the data needed to identify and quantify potential sources of sampling error (Table 4-2). It will be essential to account for these potentially significant sources of uncertainty (i.e., variance) in determining whether the current sampling design will allow EMAP-E to meet the target status and/or trends DQOs.

TABLE 4-2. Potential sources of sampling error being estimated during the first four years of EMAP-E monitoring in the Virginian Province.

Source of Error	EMAP-E Estimator
Small-scale spatial variability within the index period	Replicate stations sampled each year within each resource class
Temporal variability within the index period	Certain stations in each resource class are visited twice during the index period
Long-term temporal (interannual) variability	The same stations are visited each year (long-term trend sites)
Year-to-year temporal and spatial variability	Estimated using all random stations sampled in each resource class in each year

The target DQOs established for the EMAP program represent statements about resource class populations and do not, as stated, take into account potential sources of measurement error. Measurement error is frequently emphasized in the DQO process as an important source of uncertainty. In EMAP, measurement error may be a less significant contributor to total uncertainty than sample density. Measurement error is, however, a potentially important variable in controlling the regional responsiveness, and thus the acceptability, of individual indicators. In addition, external users of EMAP data may find that measurement error is an important source of variability that must be accounted for in addressing their own DQOs. It is therefore important for EMAP Resource Groups to control measurement error, to the extent possible, when selecting sampling methods and establish measurement quality objectives (MQOs) for each sampling method and laboratory analysis procedure. MQOs essentially represent data quality objectives that are based on control of the measurement system. They are being used to establish criteria for data acceptability because reliable error bounds cannot, at present, be established for end use of indicator response data. As a consequence, management decisions balancing the cost of higher quality data against program objectives are not presently possible. As data are accumulated on indicators and the error rates associated with their measurement at regional scales are established, it will be possible to address the target DQOs that have been established and determine the need for modifications to the sampling design and/or quality assurance program.

Measurement quality objectives for the various measurements being made in EMAP-Estuaries can be expressed in terms of accuracy, precision, and completeness requirements (Table 4-3). These MQOs were established by obtaining estimates of the most likely data quality that is achievable based on either the instrument manufacturer's specifications, scientific experience or historical data.

The MQOs presented in Table 4-3 are used as quality control criteria both in field and laboratory measurement processes to set the bounds of acceptable measurement error. Usually, DQOs or MQOs are established for five aspects of data quality: representativeness, completeness, comparability, accuracy, and precision (Stanley and Verner 1985). These terms are described in the following sections in terms of their overall applicability to the EMAP-Estuaries Program and the specific measurement systems being employed for each indicator.

TABLE 4-3. Measurement quality objectives for EMAP-Estuaries indicators. Accuracy (bias) requirements are expressed as either maximum allowable percent deviation (%) or absolute difference (± value) from the "true" value; precision requirements are expressed as maximum allowable relative percent difference (RPD) or relative standard deviation (RSD) between two or more replicate measurements. Completeness goals are the percentage of expected results to be obtained successfully.

Indicator/Data Type	Accuracy (Bias) Requirement	Precision Requirement	Completeness Goal
Sediment/tissue contaminant analyses:			
Organics	30%	30%	100%
Inorganics	15%	15%	100%
Sediment toxicity	NA	NA	100%
Benthic species composition and biomass:			
Sorting	10%	NA	100%
Counting	10%	NA	100%
Taxonomy	10%	NA	100%
Biomass	NA	10%	100%
Sediment characteristics:			
Particle size (% silt-clay) analysis	NA	10%	100%
Total organic carbon	10%	10%	100%
Acid volatile sulfide	10%	10%	100%
Water Column Characteristics:			
Dissolved oxygen	± 0.5 mg/L	10%	100%
Salinity	± 1.0 ppt	10%	100%
Depth	± 0.5 m	10%	100%
pH	± 0.2 units	NA	100%
Temperature	± 0.5 ºC	NA	100%
Total Suspended solids	NA	10%	100%
Gross pathology of fish	NA	10%	100%
Fish community composition:			
Counting	10%	NA	100%
Taxonomic identification	10%	NA	100%
Length determinations	± 5 mm	NA	100%
Fish histopathology	NA	NA	NA

4.2 REPRESENTATIVENESS

Representativeness is defined as "the degree to which the data accurately and precisely represent a characteristic of a population parameter, variation of a property, a process characteristic, or an operational condition" (Stanley and Verner, 1985). The concept of representativeness within the context of EMAP monitoring refers to the ability of the program to accurately and precisely characterize regional phenomena through the measurement of selected environmental indicators. The focus on regional phenomena requires that the EMAP design strategy emphasize accommodation of a wide range of resources. In addressing this requirement, EMAP-Estuaries has adopted a regionalization scheme to allocate the Nation's estuarine and coastal resources into manageable sampling units for collection and reporting of data. This regionalization, determined on the basis of major climatic zones and prevailing oceanic currents, consists of seven provinces within the continental United States, five provinces in Alaska, Hawaii, and the Pacific territories, and a region that comprises the Great Lakes. In addition, EMAP-Estuaries is using a classification scheme to facilitate sampling of the ecosystems within each province in proportion to their extent and abundance, thus ensuring a statistically-acceptable representation of all ecosystem types within the sampling frame. In the Virginian Province, physical dimensions (e.g., surface area and aspect ratio) are used to classify estuarine resources into three categories: large estuarine systems, large tidal rivers, and small estuarine systems. Complete descriptions of the EMAP-Estuaries regionalization and classification schemes are provided in the Near Coastal Program Plan for 1990 (Holland 1990).

The design of the EMAP-Estuaries' sampling program and the location of Virginian Province sampling sites provide the primary focus for defining the "representativeness" of population estimates for this region. In its initial planning stages, the EMAP-E program faced a choice between two general sampling approaches to meet the objective of obtaining an accurate and precise representation of estuarine resource condition at the regional scale. As described in the Near Coastal Program Plan (Holland 1990) and restated here, these two sampling approaches were: 1.) census the nation's estuarine and coastal ecosystems and important habitats on a periodic basis (e.g., every 4 years), or 2.) sample a subset of estuarine and coastal resources periodically, and use the data to make inferences about unsampled area.

The census technique is the appropriate sampling method for characterizing and assessing status and trends for some rare resources, because minimal population densities require that most of the resource must be sampled to characterize status and to measure trends (e.g., changes in abundance of rare and endangered species or habitats). The census technique is not a cost-effective or appropriate sampling approach for assessing the status and trends of broadly distributed, relatively abundant resources. EMAP-E does not have the resources to conduct a regular census of the nation's estuarine and coastal resources. Therefore, the decision was made that sampling a subset of the resources and using the information obtained about the subset to make inferences about unsampled resources is the only approach that is appropriate for EMAP-E.

The subset of resources sampled by EMAP-E could be (1) a sample which is determined, based on available scientific knowledge, to be "representative" of the range of environmental settings that exist in estuarine and coastal environments, or (2) a probability sample of estuarine and coastal resources. Collection of "representative" samples is an extreme case of stratified sampling and assumes that the data collected at the "representative" sampling locations can be extrapolated to broader spatial and temporal scales. Available scientific information is used to identify "representative" sampling locations, as well as to define the spatial scale and temporal periods that the samples represent. Periodic collection of "representative" samples is a powerful technique for measuring trends, because this approach minimizes interactions between spatial and temporal variation. Because "representative" samples can be located at any of a number of sites, they are generally easier to collect than probability samples and frequently can be located at a site for which there is existing historical data.

Unfortunately, the current scientific understanding of the environmental processes that control condition and distributions of estuarine and coastal resources is inadequate to define the bias and uncertainty associated with extrapolating environmental quality information for "representative" locations to other sites. This is especially true for data collected over broad geographic scales and long time periods. Therefore, EMAP-E employs a probability sampling approach that samples resources in proportion to their abundance and distribution and obtains unbiased estimates of resource characteristic and variability. The probability sampling approach applies systematic (e.g., grid) sampling to facilitate characterizations of spatial patterns and to encourage broad geographic coverage.

Many of the proposed parameters that EMAP-E will measure are known to exhibit large intra-annual variability, and EMAP-E lacks the resources to characterize this variability or to assess status for all seasons. Therefore, sampling will be confined to a limited portion of the year (i.e., an index period), when indicators are expected to show the greatest response to pollution stress and within-season (i.e., week-to-week) variability is expected to be small.

For most estuarine and coastal ecosystems in the Northern Hemisphere, mid-summer (July-August) is the period when ecological responses to pollution exposure are likely to be most severe. During this period, dissolved oxygen concentrations are most likely to approach stressful low values. Moreover, the cycling and adverse effects of contaminant exposure are generally greatest at the low dilution flows and high temperatures that occur in mid-summer. Therefore, summer has been selected as the most conservative (i.e., most ecologically-stressful) index period for EMAP-E.

Once unbiased quantitative information on the kinds, extent, condition and distribution of estuarine and coastal resources and associated estimates of uncertainty are known, a baseline of the status of existing conditions will be established. This baseline information will be used to develop criteria for identifying "representative" sampling sites for future sampling (e.g., trends sites, detailed studies of processes associated with deterioration and recovery, the magnitude of natural variation). This baseline will also be used to determine the "representativeness" of historical data and sampling sites (e.g., NOAA Status and Trends sites). Over the long-term, EMAP-E seeks to develop a sampling design that includes both "representative" and probability sampling, incorporating the advantages of both approaches.

The data quality attribute of "representativeness" applies not only to the overall sampling design, but also to individual measurements and samples obtained as part of EMAP-E's monitoring efforts. Holding time requirements for different types of samples ensure that analytical results are representative of conditions at the time of sampling; these requirements are specified in the individual indicator sections of this document. In addition, use of QA/QC samples which are similar in composition to samples being measured provides estimates of precision and bias that are representative of sample measurements. Therefore, as a general program objective, the types of QA documentation samples (*i.e.*, performance evaluation material) used to assess the quality of analytical data will be as representative as possible of the natural samples collected during the project with respect to both composition and concentration.

4.3 COMPLETENESS

Completeness is defined as "a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement" (Stanley and Verner 1985). EMAP-E has established a completeness goal of 100% for the various indicators being measured (Table 4-3). Given the probability-based sampling design being employed by EMAP-E, failure to achieve this goal will not preclude the within-year or between-year assessment of ecosystem condition. The major consequence of having less than 100% complete data from all expected stations is a relatively minor loss of statistical power in the areal estimate of condition, as depicted using Cumulative Distribution Functions (CDFs). The 100% completeness goal is established in an attempt to derive the maximum statistical power from the present sampling design. Based on past years' experience, failure to achieve this goal usually results from the field crew's inability to sample at some stations due to logistical barriers such as insufficient depth, inpenetrable substrate, or adverse weather conditions. In the limited number of instances where these conditions may be encountered, extensive efforts will be made to re-locate the station or re-sample the station at a later date, always in consultation with program managers at the Field Operations Center. In this way, field personnel must always strive to achieve the 100% completeness goal. In addition, established protocols for tracking samples during shipment and laboratory processing must be followed to minimize data loss following successful sample collection.

4.4 COMPARABILITY

Comparability is defined as "the confidence with which one data set can be compared to another" (Stanley and Verner 1985). Comparability of reporting units and calculations, data base management processes, and interpretative procedures must be assured if the overall goals of EMAP are to be realized. One goal of the EMAP-Estuaries program is to generate a high level of documentation for the above topics to ensure that future EMAP efforts can be made comparable. For example, both field and laboratory methods are described in full detail in manuals which will be made available to all field personnel and analytical laboratories. Field crews will undergo intensive training in a single four week session prior to the start of field work. In addition, the comparability of laboratory measurements is monitored through the interlaboratory comparison exercises and the use of field split or duplicate performance evaluation samples. The results of this comparibility monitoring will be presented and evaluated in a quality assurance

report prepared by the program's QA personnel following each year's sampling effort. Comparability will be assessed through application of appropriate statistical tests (e.g., t-tests, ANOVA), and results will be considered comparable if there are no significant differences. Failure to achieve this comparability goal will result in corrective actions which may include, but are not limited to, changes in field and laboratory methodology and/or concomitant changes in the program's QA/QC requirements.

4.5 ACCURACY (BIAS), PRECISION, AND TOTAL ERROR

The term "accuracy", which is used synonymously with the term bias in this plan, is defined as the difference between a measured value and the true or expected value, and represents an estimate of systematic error or net bias (Kirchner 1983; Hunt and Wilson 1986; Taylor 1987). Precision is defined as the degree of mutual agreement among individual measurements, and represents an estimate of random error (Kirchner 1983; Hunt and Wilson 1986; Taylor 1987). Collectively, accuracy and precision can provide an estimate of the total error or uncertainty associated with an individual measured value. Measurement quality objectives for the various indicators are expressed separately as accuracy (*i.e.*, bias) and precision requirements (Table 4-3). Accuracy and precision requirements may not be definable for all parameters due to the nature of the measurement type. For example, accuracy measurements are not possible for toxicity testing and fish pathology identifications because "true" or expected values do not exist for these measurement parameters (see Table 4-3). In order to evaluate the MQOs for accuracy and precision, various QA/QC samples will be collected and analyzed for most data collection activities. Table 4-4 presents the types of samples to be used for quality assurance/quality control for each of the various data acquisition activities except sediment and fish tissue contaminant analyses. The frequency of QA/QC measurements and the types of QA data resulting from these samples or processes are also presented in Table 4-4. Because several different types of QA/QC samples are required for the complex analyses of chemical contaminants in sediment and tissue samples, they are presented and discussed separately in Section 5 along with presentation of warning and control limits for the various chemistry QC sample types.

TABLE 4-4. Quality assurance sample types, frequency of use, and types of data generated for EMAP-Estuaries Virginian Province monitoring (see Table 5-4 for chemical analysis QA/QC sample types).

Variable	QA Sample Type or Measurement Procedure	Frequency of Use	Data Generated for Measurement Quality Definition
Sediment toxicity tests	Reference toxicant	Each experiment	Variance of replicated tests over time
Benthic Species Composition and Biomass:			
Sorting	Resort of sample	10% of each tech's work	No. animals found in resort
Sample counting and ID	Recount and ID of sorted animals	10% of each tech's work	No. of count and ID errors
Biomass	Duplicate weights	10% of samples	Duplicate results
Sediment grain size	Splits of a sample	10% of each tech's work	Duplicate results
Organic carbon and acid volatile sulfide	Duplicates and analysis of standards	Each batch	Duplicate results and standard recoveries
Dissolved Oxygen conc. (CTD)	Comparison of calibrated YSI and CTD values	Each CTD cast	Difference between CTD and YSI
Dissolved Oxygen conc. (YSI)	Comparison with Winkler value	Once per shift	Difference between YSI and Winkler value

(continued)

Table 4-4 (continued).

Variable	QA Sample Type or Measurement Procedure	Frequency of Use	Data Generated for Measurement Quality Definition
Salinity	Refractometer reading	Each CTD cast	Difference between CTD probe and refractometer readings
Temperature	Thermometer reading	Each CTD cast	Difference between probe and thermometer
Depth	Check bottom depth against depth finder	Each CTD cast	Difference from actual
pH	QC check with standard	Once each day	Difference from standard
Fish identification	Fish preserved for verification by taxonomist	Twice/crew for each species	Number of mis-identifications
Fish counts/length	Remeasured and recounted during field QA audits	One audit for each crew/season	Difference between original and recount/ remeasurement
Fish gross pathology	Specimens preserved for confirmation	At least once per crew shift	Number of mis-identifications
Fish histopathology	Confirmation by second technician	5% of slides	Number of confirmations

SECTION 5

ANALYSIS OF CHEMICAL CONTAMINANTS IN SEDIMENT AND FISH TISSUE SAMPLES

5.1 OVERVIEW

Quality assurance of chemical measurements has many diverse aspects. This section presents EMAP-Estuaries QA/QC protocols and requirements covering a range of activities, from sample collection and laboratory analysis to final validation of the resultant data. Much of the guidance provided in this section is based on protocols developed for EPA's Puget Sound Estuary Program (U.S. EPA 1989), as well as those developed over many years on the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends (NS&T) Program. This guidance is applicable to low parts per billion analyses of both estuarine sediment and tissue samples unless otherwise noted.

The EMAP-E program measures a variety of organic and inorganic contaminants in estuarine sediment and fish tissue samples (Tables 5-1 and 5-2); these compounds are the same as those measured in the NOAA NS&T Program, with a few additions. These contaminants are being measured for the purpose of environmental monitoring, with the understanding that the data will not be used for litigation purposes. Therefore, legal and contracting requirements as stringent as those used in the U.S. EPA Contract Laboratory Program, for example, have not been applied to EMAP-E. Rather, EMAP-E requires its laboratories to demonstrate comparability continuously through strict adherence to common QA/QC procedures, routine analysis of Certified Reference Materials[1], and regular participation in an on-going series of interlaboratory comparison exercises (round-robins). This is a "performance-

[1] Certified Reference Materials (CRMs) are samples in which chemical concentrations have been determined accurately using a variety of technically valid procedures; these samples are accompanied by a certificate or other documentation issued by a certifying body (*e.g.*, agencies such as the National Research Council of Canada (NRCC), U.S. EPA, U.S. Geological Survey, etc.). Standard Reference Materials (SRMs) are CRMs issued by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). A useful catalogue of marine science reference materials has been compiled by Cantillo (1992).

TABLE 5-1. Chemicals to be measured in sediments by EMAP-E Virginian Province.

Polyaromatic Hydrocarbons (PAHs)

Acenaphthene	1-methylnapthalene	
Anthracene	1-methylphenanthrene	
Benz(a)anthracene	Naphthalene	
Benzo(a)pyrene	Perylene	
Benzo(e)pyrene	Phenanthrene	
Biphenyl	Pyrene	
Chrysene	Benzo(b)fluoranthene	
Dibenz(a,h)anthracene	Acenaphthlylene	
2,6-dimethylnaphthalene	Benzo(k)fluoranthene	
Fluoranthene	Benzo(g,h,i)perylene	
Fluorene	Ideno(1,2,3-c,d)pyrene	
2-methylnaphthalene	2,3,5-trimethylnaphthalene	

18 PCB Congeners:

PCB No.	Compound name
8	2,4'-dichlorobiphenyl
18	2,2',5-trichlorobiphenyl
28	2,4,4'-trichlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl
66	2,3',4,4'-tetrachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
128	2,2',3,3',4,4'-hexachlorobiphenyl
138	2,2',3,4,4',5'-hexachlorobiphenyl
153	2,2',4,4',5,5'-hexachlorobiphenyl
170	2,2',3,3',4,4',5-heptachlorobiphenyl
180	2,2',3,4,4',5,5'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl
195	2,2',3,3',4,4',5,6-octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

Other measurements

Acid volatile sulfide
Total organic carbon
Tetra-, Tri-, Di-, and Monobutyltin

DDT and its metabolites

2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4,4'-DDT

Chlorinated pesticides other than DDT

Endrin
Aldrin
Alpha-Chlordane
Endosulfan
Trans-Nonachlor
Dieldrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (gamma-BHC)
Mirex

Major Elements

Aluminum
Iron
Manganese

Trace Elements

Antimony
Arsenic
Cadmium
Chromium
Copper
Lead
Mercury
Nickel
Selenium
Silver
Tin
Zinc

TABLE 5-2. Chemicals to be measured in fish tissue by EMAP-E Virginian Province.

DDT and its metabolites

2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4,4'-DDT

Chlorinated pesticides other than DDT

Aldrin
Alpha-Chlordane
Trans-Nonachlor
Dieldrin
Endosulfan
Endrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (gamma-BHC)
Mirex

Trace Elements

Aluminum
Arsenic
Cadmium
Chromium
Copper
Iron
Lead
Mercury
Nickel
Selenium
Silver
Tin
Zinc

Other chemicals

Tetra-, Tri-, Di- and Monobutyltin

18 PCB Congeners:

PCB No.	Compound name
8	2,4'-dichlorobiphenyl
18	2,2',5-trichlorobiphenyl
28	2,4,4'-trichlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl
66	2,3',4,4'-tetrachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
128	2,2',3,3',4,4'-hexachlorobiphenyl
138	2,2',3,4,4',5'-hexachlorobiphenyl
153	2,2',4,4',5,5'-hexachlorobiphenyl
170	2,2',3,3',4,4',5-heptachlorobiphenyl
180	2,2',3,4,4',5,5'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl
195	2,2',3,3',4,4',5,6-octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

based" approach for quality assurance of low-level contaminant analyses, involving continuous laboratory evaluation through the use of accuracy-based materials (e.g., CRMs), laboratory fortified sample matrices, laboratory reagent blanks, calibration standards, and laboratory and field replicates. The definition and use of each of these types of quality control samples are explained in later sections.

No single analytical method has been approved officially for low-level (*i.e.*, low parts per billion) analysis of organic and inorganic contaminants in estuarine sediments and fish tissue. Recommended methods for the EMAP-E program are those used in the NOAA NS&T Program (Lauenstein et al. 1993), as well as those documented in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision). Under the EMAP-E performance-based chemistry QA program, laboratories are not required to use a single, standard analytical method for each type of analysis, but rather are free to choose the best or most feasible method within the constraints of cost and equipment. Each laboratory must, however, continuously demonstrate proficiency and data comparability through routine analysis of accuracy-based performance evaluation samples and reference materials representing real-life matrices.

5.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING

Field personnel must strictly adhere to EMAP-E protocols to insure the collection of representative, uncontaminated sediment and fish tissue chemistry samples. These sample collection protocols are described in detail in the Virginian Province Field Operations Manual (Reifsteck et al. 1993). Briefly, the key aspects of quality control associated with chemistry sample collection are as follows: 1.) field personnel must be thoroughly trained in the proper use of sample collection gear and must be able to distinguish acceptable versus unacceptable sediment grab samples or fish trawls in accordance with pre-established criteria, 2.) field personnel must be thoroughly trained to recognize and avoid potential sources of sample contamination (e.g., engine exhaust, winch wires, deck surfaces, ice used for cooling), 3.) samplers and utensils which come in direct contact with the sample should be made of non-contaminating materials (e.g., glass, high-quality stainless steel and/or Teflon®) and should be thoroughly cleaned between sampling stations (e.g., Alconox® scrub followed by thorough rinse with ambient seawater or river water and final rinse with deionized water), 4.) sample containers should be of the recommended type (Table 5-3) and must be free of contaminants (i.e., carefully pre-cleaned), 5.) conditions for sample collection, preservation and holding times should be followed (Table 5-3).

Table 5-3. Summary of chemistry sample collection, preservation, and holding time conditions to be followed for EMAP-E Virginian Province monitoring.

Parameter	Container	Sample Volume	Sample Size	Sample Preservation	Max. Sample Holding Time	Max. Extract Holding Time
Sediment Metals (except Hg)	250-ml HDPE wide-mouth bottle	100 to 150 ml	100 to 150 g (approx.)	Cool, 4°C	6 months	- [a]
Sediment Hg and TOC	same as above	same as above	same as above	same as above	28 days	- [a]
Sediment Organics (including butyltins)	500-ml pre-cleaned glass wide-mouth jar	250 to 300 ml	300 g (approx.)	Cool, 4°C	14 days[b]	40 days
Sediment Acid Volatile Sulfide (AVS)	125-ml. poly-propylene wide-mouth bottle	125 ml[c]	125 g	Cool, 4°C	14 days	36 hours
Fish Tissue (Organics and In-organics)	Whole fish are placed in water-tight plastic bags	NA	NA	Freeze (-18°C)	1 year[d]	40 days

[a] No EPA criteria exist. Every effort should be made to analyze sample as soon as possible following extraction or, in the case of metals, digestion.

[b] Every effort should be made to analyze these samples as soon as possible. If extractions are not to be performed within 14 days, these samples should be frozen (-18°C) and extracted within 1 year.

[c] AVS containers should be filled to the top to minimize or eliminate headspace; containers should be capped tightly. Every effort should be made to minimize contact of the sediment with air and to analyze these samples as soon as possible.

[d] No EPA criteria exists for holding times of tissue samples. This is a maximum suggested holding time.

5.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

5.3.1 Overview

The QA/QC requirements presented in the following sections are intended to provide a common foundation for each laboratory's protocols; the resultant QA/QC data will enable an assessment of the comparability of results generated by different laboratories and different analytical procedures. It should be noted that the QA/QC requirements specified in this plan represent the minimum requirements for any given analytical method. Additional requirements which are method-specific should always be followed, as long as the minimum requirements presented in this document have been met.

The performance-based EMAP-E QA program for analytical chemistry laboratories consists of two basic elements: 1.) initial demonstration of laboratory capability (e.g., performance evaluation) and 2.) ongoing demonstration of capability. Prior to the analysis of samples, each laboratory must demonstrate proficiency in several ways: written protocols for the analytical methods to be employed for sample analysis must be submitted to the Program for review, method detection limits for each analyte must be calculated, an initial calibration curve must be established for all analytes, and acceptable performance must be shown on a known or blind accuracy-based material. Following a successful first phase, the laboratory must demonstrate its continued capabilities in several ways: participation in an on-going series of interlaboratory comparison exercises, repeated analysis of Certified Reference Materials, calibration checks, and analysis of laboratory reagent blanks and fortified samples. These steps are detailed in the following sections and summarized in Table 5-4. The sections are arranged to mirror the elements in Table 5-4 to provide easy cross-reference for the reader.

The results for the various QA/QC samples should be reviewed by laboratory personnel immediately following the analysis of each sample batch. These results then should be used to determine when warning and control limit criteria have not been met and corrective actions must be taken, before processing a subsequent sample batch. When warning limit criteria have not been met, the laboratory is not obligated to halt analyses, but the analyst(s) is advised to investigate the cause of the exceedance. When control limit criteria are not met, specific corrective actions are required before the analyses may proceed. Warning and control limit criteria and recommended frequency of analysis for each QA/QC element or sample type required in the EMAP-E program also are summarized in Table 5-4.

TABLE 5-4. Key elements of laboratory quality control for EMAP-Estuaries chemical analyses (see text for detailed explanations).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
1.) Initial Demonstration of Capability (Prior to Analysis of Samples):			
- Instrument Calibration	NA	NA	Initial and then prior to analyzing each batch of samples
- Calculation of Method Detection Limits	Must be equal to or less than target values (see Table 5-5)		At least once each year
- Blind Analysis of Accuracy-Based Material	NA	NA	Initial
2.) On-going Demonstration of Capability:			
- Blind Analysis of Interlaboratory Comparison Exercise Samples	NA	NA	Regular intervals throughout the year
- Continuing Calibration Checks using Calibration Standard Solutions	NA	should be within ±15% of initial calibration on average for all analytes, not to exceed ±25% for any one analyte	At a minimum, middle and end of each sample batch

(continued)

TABLE 5-4 (continued).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
- Analysis of Certified Reference Material (CRM) or Laboratory Control Material (LCM):			One with each batch of samples
Precision (see NOTE 1):	NA	Value obtained for each analyte should be within 3s control chart limits	Value plotted on control chart after each analysis of the CRM
Relative Accuracy (see NOTE 2):			
PAHs	Lab's value should be within ±25% of true value on average for all analytes; not to exceed ±30% of true value for more than 30% of individual analytes	Lab's value should be within ±30% of true value on average for all analytes; not to exceed ±35% of true value for more than 30% of individual analytes	
PCBs/pesticides	same as above	same as above	
inorganic elements	Lab should be within ±15% of true value for each analyte	Lab should be within ±20% of true value for each analyte	

NOTE 1: The use of control charts to monitor precision for each analyte of interest should follow generally accepted practices (*e.g.*, Taylor 1987 and section 3.2.5 of this document). Upper and lower control limits, based on 99% confidence intervals around the mean, should be updated at regular intervals.

NOTE 2: "True" values in CRMs may be either "certified" or "non-certified" (it is recognized that absolute accuracy can only be assessed using certified values, hence the term relative accuracy). Relative accuracy is computed by comparing the laboratory's value for each analyte against either end of the range of values (*i.e.*, 95% confidence limits) reported by the certifying agency. The laboratory's value must be within ±35% of either the upper or lower 95% confidence interval value. Accuracy control limit criteria only apply for analytes having CRM concentrations ≥10 times the laboratory's MDL.

(continued)

TABLE 5-4 (continued).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
- Laboratory Reagent Blank	Analysts should use best professional judgement if analytes are detected at <3 times the MDL	No analyte should be detected at >3 times the MDL	One with each batch of samples
- Laboratory Fortified Sample Matrix (Matrix Spike)	NA	Recovery should be within the range 50% to 120% for at least 80% of the analytes	At least 5% of total number of samples
NOTE: Samples to be spiked should be chosen at random; matrix spike solutions should contain all the analytes of interest. The final spiked concentration of each analyte in the sample should be at least 10 times the calculated MDL.			
- Laboratory Fortified Sample Matrix Duplicate (Matrix Spike Duplicate)	NA	RPD[1] must be ≤ 30 for each analyte	Same as matrix spike
- Field Duplicates (Field Splits)	NA	NA	5% of total number of samples
- Internal Standards (Surrogates)	NA	Recovery must be within the range 30% to 150%	Each sample
- Injection Internal Standards	Lab develops its own	Lab develops its own	Each sample

[1] RPD = Relative percent difference between matrix spike and matrix spike duplicate results (see appropriate section for equation).

5.3.2 Initial Demonstration of Capability

Instrument Calibration

Equipment should be calibrated prior to the analysis of each sample batch, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended control limit criteria (Table 5-4). All calibration standards should be traceable to a recognized organization for the preparation and certification of QA/QC materials (*e.g.*, National Institute of Standards and Technology, U.S. Environmental Protection Agency, etc.). Calibration curves must be established for each element and batch analysis from a calibration blank and a minimum of three analytical standards of increasing concentration, covering the range of expected sample concentrations. The calibration curve should be well-characterized and must be established prior to the analysis of samples. Only data which results from quantification within the demonstrated working calibration range may be reported by the laboratory (*i.e.*, quantification based on extrapolation is not acceptable). Samples outside the calibration range should be diluted or concentrated, as appropriate, and reanalyzed.

Initial Documentation of Method Detection Limits

Analytical chemists have coined a variety of terms to define "limits" of detectability; definitions for some of the more commonly-used terms are provided in Keith *et al*. (1983) and in Keith (1991). In the EMAP-E program, the Method Detection Limit (MDL) will be used to define the analytical limit of detectability. The MDL represents a quantitative estimate of low-level response detected at the maximum sensitivity of a method. The Code of Federal Regulations (40 CFR Part 136) gives the following rigorous definition: "the MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." Confidence in the apparent analyte concentration increases as the analyte signal increases above the MDL.

Each EMAP-E analytical laboratory must calculate and report an MDL for each analyte of interest in each matrix of interest (sediment or tissue) prior to the analysis of field samples for a given year. Each laboratory is required to follow the procedure specified in 40 CFR Part 136 (Federal Register, Oct. 28, 1984) to calculate MDLs for each

analytical method employed. The matrix and the amount of sample (*i.e.*, dry weight of sediment or tissue) used in calculating the MDL should match as closely as possible the matrix of the actual field samples and the amount of sample typically used. In order to ensure comparability of results among different laboratories, MDL target values have been established for the EMAP-E program (Table 5-5). The initial MDLs reported by each laboratory should be equal to or less than these specified target values before the analysis of field samples may proceed. Each laboratory must periodically (*i.e.*, at least once each year) re-evaluate its MDLs for the analytical methods used and the sample matrices typically encountered.

TABLE 5-5. Target method detection limits for EMAP-Estuaries analytes.

INORGANICS **(NOTE: concentrations in µg/g (ppm), dry weight)**

	Tissue	Sediments
Aluminum	10.0	1500
Antimony	not measured	0.2
Arsenic	2.0	1.5
Cadmium	0.2	0.05
Chromium	0.1	5.0
Copper	5.0	5.0
Iron	50.0	500
Lead	0.1	1.0
Manganese	not measured	1.0
Mercury	0.01	0.01
Nickel	0.5	1.0
Selenium	1.0	0.1
Silver	0.01	0.01
Tin	0.05	0.1
Zinc	50.0	2.0

ORGANICS **(NOTE: concentrations in ng/g (ppb), dry weight)**

	Tissue	Sediments
PAHs	not measured	10
PCB congeners	2.0	1.0
Chlorinated pesticides	2.0	1.0

Initial Blind Analysis of a Representative Sample

A representative sample matrix which is uncompromised, homogeneous and contains the analytes of interest at concentrations of interest will be provided to each analytical laboratory new to the EMAP-E program; this sample will be used to evaluate laboratory performance prior to the analysis of field samples. The sample used for this initial demonstration of laboratory capability typically will be distributed blind (*i.e.*, the laboratory will not know the concentrations of the analytes of interest) as part of the interlaboratory comparison exercises. Based on results that have typically been attained by experienced EMAP-Estuaries laboratories, a new laboratory's performance generally will be considered acceptable if its submitted values are within ±30% (for organic analyses) and ±20% (for inorganic analyses) of the known concentration of each analyte of interest in the sample. These criteria apply only for analyte concentrations equal to or greater than 10 times the MDL established by the laboratory. If the results for the initial analysis fail to meet these criteria, the laboratory will be required to repeat the analysis until the performance criteria are met, prior to the analysis of real samples.

5.3.3 On-going Demonstration of Capability

Participation in Interlaboratory Comparison Exercises

Through an interagency agreement, NOAA's NS&T Program and EPA's EMAP-E program jointly sponsor an on-going series of interlaboratory comparison exercises (round-robins). All EMAP-E analytical laboratories are required to participate in these exercises, which are conducted jointly by the National Institute of Standards and Technology (NIST) and the National Research Council of Canada (NRCC). These exercises provide a tool for continuous improvement of laboratory measurements by helping analysts identify and resolve problems in methodology and/or QA/QC. The results of these exercises also are used to evaluate both the individual and collective performance of the participating analytical laboratories on a continuous basis. The EMAP-E laboratories are required to initiate corrective actions if their performance in these comparison exercises falls below certain pre-determined minimal standards, described in later sections.

Typically, three or four different exercises are conducted over the course of a year. In a typical exercise, either NIST or NRCC will distribute performance evaluation samples in common to each laboratory, along with detailed

instructions for analysis. A variety of performance evaluation samples have been utilized in the past, including accuracy-based solutions, sample extracts, and representative matrices (*e.g.*, sediment or tissue samples). Laboratories are required to analyze the sample(s) "blind" and must submit their results in a timely manner both to the EMAP-E QA Coordinator, as well as to either NIST or NRCC (as instructed). Laboratories which fail to maintain acceptable performance may be required to provide an explanation and/or undertake appropriate corrective actions. At the end of each calendar year, coordinating personnel at NIST and NRCC hold a QA workshop to present and discuss the comparison exercise results. Representatives from each laboratory are expected to participate in the annual QA workshops, which provide a forum for discussion of analytical problems brought to light in the comparison exercises.

Routine Analysis of Certified Reference Materials or Laboratory Control Materials

Certified Reference Materials (CRMs) generally are considered the most useful QC samples for assessing the accuracy of a given analysis (*i.e.*, the closeness of a measurement to the "true" value). Certified Reference Materials can be used to assess accuracy because they have "certified" concentrations of the analytes of interest, as determined through replicate analyses by a reputable certifying agency using two independent measurement techniques for verification. In addition, the certifying agency may provide "non-certified" or "informational" values for other analytes of interest. Such values are determined using a single measurement technique, which may introduce unrecognized bias. Therefore, non-certified values must be used with caution in evaluating the performance of a laboratory using a method which differs from the one used by the certifying agency. A list of reference materials commonly used by EMAP-E laboratories is presented in Table 5-6.

A Laboratory Control Material (LCM) is similar to a Certified Reference Material in that it is a homogeneous matrix which closely matches the samples being analyzed. A "true" LCM is one which is prepared (*i.e.*, collected, homogenized and stored in a stable condition) strictly for use in-house by a single laboratory. Alternately, the material may be prepared by a central laboratory and distributed to others (so-called regional or program control materials). Unlike CRMs, concentrations of the analytes of interest in LCMs are not certified but are based upon a statistically valid number of replicate analyses by one or several laboratories. In practice, this material can be used to assess the precision (*i.e.*, consistency) of a single laboratory, as well as to determine the degree of comparability among different

Table 5-6. Certified Reference Materials commonly used by EMAP-E laboratories. SRMs are available from NIST (phone 301-975-6776); all other reference materials listed are available from NRC (phone 613-993-2359).

Calibration Solutions:

SRM 1491	Aromatic Hydrocarbons in Hexane/Toluene
SRM 1492	Chlorinated Pesticides in Hexane
SRM 1493	Chlorinated Biphenyl Congeners in 2,2,4-Trimethylpentane
SRM 2260	Aromatic Hydrocarbons in Toluene
SRM 2261	Chlorinated Pesticides in Hexane
SRM 2262	Chlorinated Biphenyl Congeners in 2,2,4-Trimethylpentane

Environmental Matrices (Organics):

SRM 1941a	Organics in Marine Sediment
SRM 1974	Organics in Mussel Tissue (Mytilus edulis)

Environmental Matrices (Inorganics):

SRM 1646	Estuarine Sediment	BCSS-1	Marine Sediment
MESS-1	Estuarine Sediment	PACS-1	Harbor Sediment
BEST-1	Marine Sediment	DORM-1	Dogfish Muscle
DOLT-1	Dogfish Liver	SRM 1566a	Oyster Tissue

laboratories. If available, LCMs may be preferred for routine (*i.e.*, day to day) analysis because CRMs are relatively expensive. However, CRMs still must be analyzed at regular intervals (*e.g.*, monthly or quarterly) to provide a check on accuracy.

Routine analysis of Certified Reference Materials or, when available, Laboratory Control Materials represents a particularly vital aspect of the "performance-based" EMAP-E QA philosophy. At least one CRM or LCM must be analyzed along with each batch of 25 or fewer samples (Table 5-4). For CRMs, both the certified and non-certified concentrations of the target analytes should be known to the analyst(s) and should be used to provide an immediate check on performance before proceeding with a subsequent sample batch. Performance criteria for both precision and accuracy have been established for analysis of CRMs or LCMs (Table 5-4); these criteria are discussed in detail in the following paragraphs. If the laboratory fails to meet either the precision or accuracy control limit criteria for a given

analysis of the CRM or LCM, the data for the entire batch of samples is suspect. Calculations and instruments should be checked; the CRM or LCM may have to be reanalyzed (*i.e.*, reinjected) to confirm the results. If the values are still outside the control limits in the repeat analysis, the laboratory is required to find and eliminate the source(s) of the problem and repeat the analysis of that batch of samples until control limits are met, before continuing with further sample processing. The results of the CRM or LCM analysis should never be used by the laboratory to "correct" the data for a given sample batch.

Precision criteria: Each laboratory is expected to maintain control charts for use by analysts in monitoring the overall precision of the CRM or LCM analyses. Upper and lower control chart limits (*e.g.*, warning limits and control limits) should be updated at regular intervals; control limits based on 99% percent confidence intervals around the mean are recommended. Following the analysis of all samples in a given year, an RSD (relative standard deviation, a.k.a. coefficient of variation) will be calculated for each analyte of interest in the CRM. Based on typical results obtained by experienced analysts, an overall RSD of less than 30% will be considered acceptable precision for each analyte having a CRM concentration $\geq$10 times the laboratory's MDL. Failure to meet this goal will result in a thorough review of the laboratory's control charting procedures and analytical methodology to determine if improvements in precision are possible.

Accuracy criteria: The "absolute" accuracy of an analytical method can be assessed using CRMs only when certified values are provided for the analytes of interest. However, the concentrations of many analytes of interest to EMAP-E are provided only as non-certified values in some of the more commonly-used CRMs. Therefore, control limit criteria are based on "relative accuracy", which is evaluated for each analysis of the CRM or LCM by comparison of a given laboratory's values relative to the "true" or "accepted" values in the LCM or CRM. In the case of CRMs, this includes both certified and noncertified values and encompasses the 95% confidence interval for each value as described in Table 5-4.

Based on typical results attained by experienced analysts in the past, accuracy control limit criteria have been established both for individual compounds and combined groups of compounds (Table 5-4). There are two combined groups of compounds for the purpose of evaluating relative accuracy for organic analyses: PAHs and PCBs/pesticides. The laboratory's value should be within ±30% of the true value on average for each combined group of organic compounds, and the laboratory's value should be within ±35% of either the upper or lower 95% confidence limit for

at least 70% of the individual compounds in each group. For inorganic analyses, the laboratory's value should be within ±20% of either the upper or lower 95% confidence limit for each analyte of interest in the CRM. Due to the inherent variability in analyses near the method detection limit, control limit criteria for relative accuracy only apply to analytes having CRM true values which are ≥10 times the MDL established by the laboratory.

Continuing Calibration Checks

The initial instrument calibration performed prior to the analysis of each batch of samples is checked through the analysis of calibration check samples (*i.e.*, calibration standard solutions) inserted as part of the sample stream. Calibration standard solutions used for the continuing calibration checks should contain all the analytes of interest. At a minimum, analysis of the calibration check solution should occur somewhere in the middle and at the end of each sample batch. Analysts should use best professional judgement to determine if more frequent calibration checks are necessary or desirable.

If the control limit for analysis of the calibration check standard is not met (Table 5-4), the initial calibration will have to be repeated. If possible, the samples analyzed before the calibration check sample that failed the control limit criteria should be reanalyzed following the recalibration. The laboratory should begin by reanalyzing the last sample analyzed before the calibration standard which failed. If the relative percent difference (RPD) between the results of this reanalysis and the original analysis exceeds 30 percent, the instrument is assumed to have been out of control during the original analysis. If possible, reanalysis of samples should progress in reverse order until it is determined that there is less than 30 RPD between initial and reanalysis results. Only the re-analysis results should be reported by the laboratory. If it is not possible or feasible to perform reanalysis of samples, all earlier data (*i.e.*, since the last successful calibration control check) is suspect. In this case, the laboratory should prepare a narrative explanation to accompany the submitted data.

Laboratory Reagent Blank

Laboratory reagent blanks (also called method blanks or procedural blanks) are used to assess laboratory contamination during all stages of sample preparation and analysis. For both organic and inorganic analyses, one laboratory reagent blank should be run in every sample batch. The reagent blank should be processed through the

entire analytical procedure in a manner identical to the samples. Warning and control limits for blanks (Table 5-4) are based on the laboratory's method detection limits as documented prior to the analysis of samples. A reagent blank concentration between the MDL and 3 times the MDL for one or more of the analytes of interest should serve as a warning limit requiring further investigation based on the best professional judgement of the analyst(s). A reagent blank concentration equal to or greater than 3 times the MDL for one or more of the analytes of interest requires definitive corrective action to identify and eliminate the source(s) of contamination before proceeding with sample analysis.

Internal Standards

Internal standards (commonly referred to as "surrogates", "surrogate spikes" or "surrogate compounds") are compounds chosen to simulate the analytes of interest in organic analyses. The internal standard represents a reference analyte against which the signal from the analytes of interest is compared directly for the purpose of quantification. Internal standards must be added to each sample, including QA/QC samples, prior to extraction. The reported concentration of each analyte **should be adjusted to correct for the recovery of the internal standard**, as is done in the NOAA National Status and Trends Program. The internal standard recovery data therefore should be carefully monitored; each laboratory must report the percent recovery of the internal standard(s) along with the target analyte data for each sample. If possible, isotopically-labeled analogs of the analytes should be used as internal standards.

Control limit criteria for internal standard recoveries are provided in Table 5-4. Each laboratory should set its own warning limit criteria based on the experience and best professional judgement of the analyst(s). It is the responsibility of the analyst(s) to demonstrate that the analytical process is always "in control" (*i.e.*, highly variable internal standard recoveries are not acceptable for repeat analyses of the same certified reference material and for the matrix spike/matrix spike duplicate).

Injection Internal Standards

For gas chromatography (GC) analysis, injection internal standards (also referred to as "internal standards" by some analysts) are added to each sample extract just prior to injection to enable optimal quantification, particularly of complex extracts subject to retention time shifts relative to the analysis of standards. Injection internal standards

are essential if the actual recovery of the internal standards added prior to extraction is to be calculated. The injection internal standards also can be used to detect and correct for problems in the GC injection port or other parts of the instrument. The compounds used as injection internal standards must be different from those already used as internal standards. The analyst(s) should monitor injection internal standard retention times and recoveries to determine if instrument maintenance or repair, or changes in analytical procedures, are indicated. Corrective action should be initiated based on the experience of the analyst(s) and not because warning or control limits are exceeded. Instrument problems that may have affected the data or resulted in the reanalysis of the sample should be documented properly in logbooks and internal data reports and used by the laboratory personnel to take appropriate corrective action.

Matrix Spike and Matrix Spike Duplicate

A laboratory fortified sample matrix (commonly called a matrix spike, or MS) and a laboratory fortified sample matrix duplicate (commonly called a matrix spike duplicate, or MSD) will be used both to evaluate the effect of the sample matrix on the recovery of the compound(s) of interest and to provide an estimate of analytical precision. A minimum of 5% of the total number of samples submitted to the laboratory in a given year should be selected at random for analysis as matrix spikes/matrix spike duplicates. Each MS/MSD sample is first homogenized and then split into three subsamples. Two of these subsamples are fortified with the matrix spike solution and the third subsample is analyzed as is to provide a background concentration for each analyte of interest. The matrix spike solution should contain all the analytes of interest. The final spiked concentration of each analyte in the sample should be at least 10 times the MDL for that analyte, as previously calculated by the laboratory.

Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the sediment samples analyzed during the project. If the percent recovery for any analyte in the MS or MSD is less than the recommended warning limit of 50 percent, the chromatograms and raw data quantitation reports should be reviewed. If an explanation for a low percent recovery value is not discovered, the instrument response may be checked using a calibration standard. Low matrix spike recoveries may be a result of matrix interferences and further instrument response checks may not be warranted, especially if the low recovery occurs in both the MS and MSD and the other QC samples in the batch indicate that the analysis was "in control". An

explanation for low percent recovery values for MS/MSD results should be discussed in a cover letter accompanying the data package. Corrective actions taken and verification of acceptable instrument response must be included.

Analysis of the MS/MSD also is useful for assessing laboratory precision. The relative percent difference (RPD) between the MS and MSD results should be less than 30 for each analyte of interest (see Table 5-4). The RPD is calculated as follows:

$$RPD = \frac{(C1 - C2)}{(C1 + C2)/2} \times 100$$

where: C1 is the larger of the duplicate results for a given analyte
C2 is the smaller of the duplicate results for a given analyte

If results for any analytes do not meet the RPD $\leq$ 30% control limit criteria, calculations and instruments should be checked. A repeat analysis may be required to confirm the results. Results which repeatedly fail to meet the control limit criteria indicate poor laboratory precision. In this case, the laboratory is obligated to halt the analysis of samples and eliminate the source of the imprecision before proceeding.

Field Duplicates and Field Splits

For the EMAP-E program, sediment will be collected at each station using a grab sampler. Each time the sampler is retrieved, the top 2 cm of sediment (approximately) will be scraped off, placed in a large mixing container and homogenized, until a sufficient amount of material has been obtained. At six pre-selected stations (one for each field crew), the homogenized material will be placed in four separate sample containers for subsequent chemical analysis. Two of the sample containers will be submitted as blind field duplicates to the primary analytical laboratory. The other two containers, also called field duplicates, will be sent blind to a second laboratory. Together, the two pairs of duplicates are called field splits. The analysis of the field duplicates will provide an assessment of single laboratory precision. The analysis of the field duplicates and field splits will provide an assessment of both inter- and intra-laboratory precision.

5.4 OTHER SEDIMENT MEASUREMENTS

The preceding sections presented QA/QC requirements covering laboratory analysis of sediment and fish tissue samples for organics (i.e., PAHs, PCBs and chlorinated pesticides) and inorganics (i.e., metals). In addition to these "conventional" contaminants, EMAP-E laboratories are required to measure several ancillary sediment parameters, such as total organic carbon (TOC), acid volatile sulfide (AVS), and tri-, di- and monobutyltin (TBT, DBT, MBT) concentrations. The laboratory QA/QC requirements associated with these "other sediment measurements" are presented in the following sections.

5.4.1 Total Organic Carbon

As a check on precision, each laboratory should analyze at least one total organic carbon (TOC) sample in duplicate for each batch of 25 or fewer samples. Based on typical results attained by experienced analysts, the relative percent difference (RPD) between the two duplicate measurements should be less than 20%. If this control limit is exceeded, analysis of subsequent sample batches should stop until the source of the discrepancy is determined and the system corrected.

At least one certified reference material (CRM) or, if available, one laboratory control material (LCM) should be analyzed along with each batch of 25 or fewer TOC samples. Any one of several marine sediment CRMs distributed by the National Research Council of Canada's Marine Analytical Chemistry Standards Program (*e.g.*, the CRMs named "BCSS-1", "MESS-1" and "PACS-1", see Table 5-6) have certified concentrations of total carbon and are recommended for this use. Prior to analysis of actual samples, it is recommended that each laboratory perform several total organic carbon analyses using a laboratory control material or one of the aforementioned CRMs to establish a control chart (the values obtained by the laboratory for total organic carbon should be slightly less than the certified value for total carbon in the CRM). The control chart then should be used to assess the laboratory's precision for subsequent analyses of the LCM or CRM with each sample batch. In addition, a method blank should be analyzed with each sample batch. Total organic carbon concentrations should be reported as μg/g (ppm) dry weight of the unacidified sediment sample. Data reported for each sample batch should include QA/QC sample results (duplicates, CRMs or LCMs, and method blanks). Any factors that may have influenced data quality should be discussed in a cover letter accompanying the submitted data, both on paper and in electronic file format (i.e., text file).

5.4.2 Acid Volatile Sulfide

Quality control of acid volatile sulfide (AVS) measurements is achieved through the routine analysis of a variety of QA/QC samples. These are outlined in the following section and described in full detail in the EMAP-E Laboratory Methods Manual (U.S. EPA, in preparation). Prior to the analysis of samples, the laboratory must establish a calibration curve and determine a limit of reliable detection for sulfide for the analytical method being employed. Following this, laboratory performance will be assessed through routine analysis of laboratory duplicates, calibration check standards, laboratory fortified blanks (*i.e.*, spiked blanks), and laboratory fortified sample matrices (*i.e.*, matrix spikes).

One sample in every batch of 25 or fewer samples should be analyzed in duplicate as a check on laboratory precision. Based on typical results attained by experienced analysts, the relative percent difference (RPD) between the two analyses should be less than 20%. If the RPD exceeds 20%, a third analysis should be performed. If the relative standard deviation of the three determined concentrations exceeds 20%, the individual analyses should be examined to determine if non-random errors may have occurred. As previously discussed, field duplicates and splits also will be collected for AVS determination to assess both inter- and intra-laboratory precision.

Due to the instability of acid volatile sulfides to drying and handling in air, CRMs have not been developed for assessing overall measurement accuracy. Therefore, each laboratory must analyze at least one calibration check standard, one laboratory fortified blank and one laboratory fortified sample matrix in each batch of 25 or fewer samples as a way of determining the accuracy of each step entailed in performing the analysis. The concentration of sulfide in each of these three types of accuracy check samples will be known to the analyst; the calculated concentration of sulfide in each sample should be within ± 15% of the known concentration.

If the laboratory is not within ± 15% of the known concentration for the calibration check solution, instruments used for AVS measurement must be recalibrated and/or the stock solutions redetermined by titration. If the laboratory fails to achieve the same accuracy (within ± 15% of the true value) for AVS in the laboratory fortified blank, sources of error (*e.g.*, leaks, excessive gas flows, poor sample-acid slurry agitation) should be determined for the analytical system prior to continuing. If AVS recovery falls outside the 85% to 115% range for the matrix spike, the system should be evaluated for sources of error and the analysis should be repeated. If recovery remains

unacceptable, it is possible that matrix interferences are occurring. If possible, the analysis should be repeated using smaller amounts of sample to reduce the interferant effects. Results for all QA/QC samples (duplicates, calibration check standards, spiked blanks and matrix spikes) should be submitted by the laboratory as part of the data package for each batch of samples, along with a narrative explanation for results outside control limits.

5.4.3 Butyltins

Assessment of the distribution and environmental impact of butyltin species of interest to the EMAP-E program (tributyltin, dibutyltin and monobutyltin) requires their measurement in marine sediment and tissue samples at trace levels. Quality control of these measurements consists of checks on laboratory precision and accuracy. One laboratory reagent blank must be run with each batch of 25 or fewer samples. A reagent blank concentration between the MDL and 3 times the MDL should serve as a warning limit requiring further investigation based on the best judgement of the analyst(s). A reagent blank concentration equal to or greater than 3 times the MDL requires corrective action to identify and eliminate the source(s) of contamination, followed by reanalysis of the samples in the associated batch.

One laboratory fortified sample matrix (commonly called a matrix spike) or laboratory fortified blank (*i.e.*, spiked blank) should be analyzed along with each batch of 25 or fewer samples to evaluate the recovery of the butyltin species of interest. The butyltins should be added at 5 to 10 times their MDLs as previously calculated by the laboratory. If the percent recovery for any of the butyltins in the matrix spike or spiked blank is outside the range 70 to 130 percent, analysis of subsequent sample batches should stop until the source of the discrepancy is determined and the system corrected.

The NRCC sediment reference material "PACS-1", which has certified concentrations of the three butyltin species of interest, also should be analyzed along with each batch of 25 or fewer sediment samples as a check on accuracy and reproducibility (*i.e.*, batch-to-batch precision). If values obtained by the laboratory for butyltins in "PACS-1" are not within ±30% of the certified values, the data for the entire batch of samples is suspect. Calculations and instruments should be checked; the CRM may have to be reanalyzed to confirm the results. If the values are still outside the control limits in the repeat analysis, the laboratory is required to determine the source(s) of the problem and repeat the analysis of that batch of samples until control limits are met, before continuing with further sample processing.

5.5 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

5.5.1 Sample Tracking

EMAP-E information management personnel have developed a comprehensive system for barcode labeling of sample containers, recording sampling information in the field and tracking sample shipments. A complete description of this system is provided in the EMAP-E Information Management Plan (Adams et al. 1993) and also summarized in Section 11 of this plan. Each analytical laboratory must designate a sample custodian, authorized to check the condition of and sign for incoming field samples, obtain documents of shipment and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the Province Information Management center. The use of barcode labels and readers provided by the Province will facilitate this process. Laboratory personnel should be aware of the required sample holding times and conditions (see Table 5-3), and the laboratory must have clearly-defined and documented custody procedures for sample handling, storage, and disbursement.

5.5.2 Data Reporting Requirements

As previously indicated, laboratory personnel must verify that the measurement process was "in control" (i.e., all specified QA/QC requirements were met) for each batch of samples before proceeding with the analysis of a subsequent batch. In addition, each laboratory must establish a system for detecting and eliminating transcription and/or calculation errors prior to reporting data. It is recommended that an individual not involved directly in sample processing be designated as laboratory QA Officer to perform these verification checks independent of day-to-day laboratory operations.

Only data which has met QA requirements should be submitted by the laboratory. When QA requirements have not been met, the samples should be reanalyzed and only the results of the reanalysis should be submitted, provided they are acceptable. Each data package should consist of the following:

- A cover letter, both on paper and in electronic file format, providing a brief description of the procedures and instrumentation used (including the procedure(s) used to calculate MDLs), as well as a narrative explanation of analytical problems (if any) or failure(s) to meet quality control limits.

- Tabulated results in hard copy form, including sample size, wet weight, dry weight, and concentrations of the analytes of interest (reported in units identified to three significant figures unless otherwise justified). Concentration units should be ng/g or μg/g (dry weight) for sediment or tissue. The results should be checked for accuracy and the report signed by the laboratory manager or designee.

- Tabulated results in computer-readable form (e.g., diskette) included in the same shipment as the hard copy data, but packaged in a diskette mailer to prevent damage. Presently, there are three acceptable formats for computer-readable data, descripions of which are available upon request from the Province Information Manager: 1.) the EPA Standard Format specified in EPA Order 2180.2 ("Data Standards for the Electronic Transmission of Laboratory Measurement Results"), 2.) ASCII text files in a format specified by the Province Information Manager, or 3.) any format agreed upon by the submitting laboratory and the Province Information Manager. If data are not delivered in one of these formats, the data package will be considered incomplete and will not be accepted.

- Tabulated method detection limits achieved for the samples.

- Results for all QA/QC samples (*e.g.*, CRMs, calibration check samples, blanks, matrix spike/matrix spike duplicates, etc.) must be submitted by the laboratory as part of the data package for each batch of samples analyzed. The laboratory must provide a "batch number" as a way to link samples from a given batch or analytical set with their accompanying QA/QC samples. The laboratory should denote QA/QC samples using the codes (abbreviations) and reporting units specified in Table 5-7.

Laboratories are responsible for assigning only two data qualifier codes or "flags" to the submitted data. If an analyte is not detected, the laboratory should report the result either as "ND" or else leave the "RESULT" field empty, followed by the letter "a" in the "QACODE" field and the method detection limit (MDL) in the "MDL" field. The "a" code has the following meaning: "The analyte was not detected. The detection limit (MDL) is reported as a separate variable." If a quantifiable signal is observed, the laboratory should report a concentration for the analyte;

TABLE 5-7. Codes for denoting QA/QC samples in submitted data packages.

Code	Description	Unit of Measure
CLC	Continuing Calibration Check Sample	Percent recovery
LRB	Lab Reagent Blank	varies
LCM	Lab Control Material	μg/g or ng/g dry wt.
LCMPR	Lab Control Material % Recovery	Percent Recovery
LF1	Lab Spiked Sample- 1st Member	μg/g or ng/g dry wt.
LF1PR	Lab Spiked Sample- 1st Mem. % Rec.	Percent Recovery
LF2	Lab Spiked Sample- 2nd Member	μg/g or ng/g dry wt.
LF2PR	Lab Spiked Sample- 2nd Mem. % Rec.	Percent Recovery
MSDRPD	Rel % Difference: LF1 to LF2	Percent
LFB	Lab Fortified Blank	Percent Recovery
LSFPR	Lab Spiked Sample % Rec.	Percent Recovery
LDRPD	Lab Duplicate Relative % Diff.	Percent

the data qualifier code "b" then should be used to flag any reported values which are below the laboratory's MDL. The "b" code has the following meaning: "The reported concentration is below or equal to the detection limit. The detection limit (MDL) is reported as a separate variable."

There may be a limited number of situations where sample re-analysis is not possible or practical (*i.e.*, minor exceedance of a single control limit criteria). The laboratory is expected to provide a detailed explanation of any factors affecting data quality or interpretation; this explanation should be in the form of a cover letter, both on paper and in electronic file format (i.e., text file) accompanying each submitted data package. The narrative explanation is in lieu of additional data qualifier codes supplied by the laboratory (other than the "a" and "b" codes). Over time, depending on the nature of these narrative explanations, the EMAP-E program expects to develop a limited list of codes for qualifying data in the database (in addition to the "a" and "b" codes).

5.5.3 Data Evaluation Procedures

It is the responsibility of the Province Manager to acknowledge initial receipt of the data package(s), verify that the four data evaluation steps identified in the following paragraph are completed, notify the analytical laboratory

of any additional information or corrective actions deemed necessary as a result of the Province's data evaluation and, following satisfactory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for a team of individuals (e.g., the Province QA Coordinator and/or analytical chemists on the Province staff) to assist the Province Manager in technical evaluation of the submitted data packages. While the Province Manager has ultimate responsibility for maintaining official contact with the analytical laboratory and verifying that the data evaluation process is completed, it is the responsibility of the Province QA Coordinator to closely monitor and formally document each step in the process as it is completed. This documentation should be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist should be supplemented with detailed memos to the project file outlining any concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package should commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten and (if holding times have been exceeded) can sometimes limit options for reanalysis. The following steps are to be followed and documented in evaluating EMAP-E chemistry data:

1.) Checking data completeness (verification)
2.) Assessing data quality (validation)
3.) Assigning data qualifier codes
4.) Taking final actions

The specific activities required to complete each of these steps are illustrated in Figure 5-1 and described in the following sections, which are adopted in large part from the document "A Project Manager's Guide to Requesting and Evaluating Chemical Analyses" (EPA 1991).

Checking Data Completeness

The first part of data evaluation is to verify that all required information has been provided in the data package. On the EMAP-E program, this should include the following specific steps:

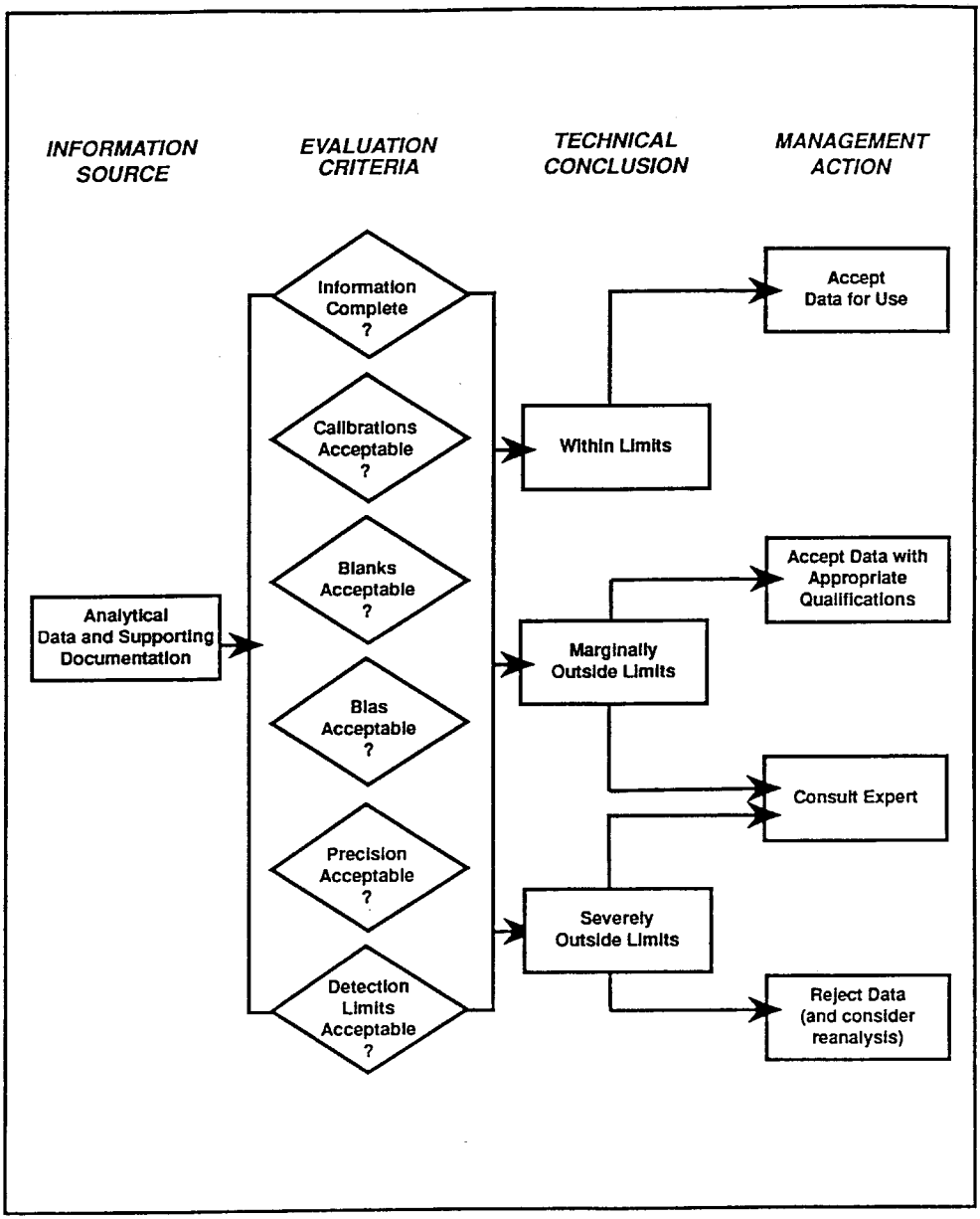

Figure 5-1. Steps to be followed in the assessment and evaluation of EMAP-E chemistry data (from U.S. EPA 1991).

- Province personnel should verify that the package contains the following: narrative explanations signed by the laboratory manager, hard copies of all results (including QA/QC results), and accompanying computer diskettes.

- The electronic data file(s) should be parsed and entered into the EMAP Province database to verify that the correct format has been supplied.

- Once the data have been entered into the Province database, automated checks should be run to verify that results have been reported for all expected samples and all analytes.

The Province Manager should contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory should provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Assessing Data Quality

Data validation, or the process of assessing data quality, can begin after Province personnel have determined that the data package is complete. Normally, the first major part of validation involves checking 100-percent of the data for any possible errors resulting from transcription of tabulated results, misidentification or miscalculations. However, EMAP-E laboratories are expected to submit data which already has been tabulated and checked 100% for accuracy, and the raw data reports needed by Province personnel to perform these checks (e.g., chromatograms, original quantitation reports) are not submitted as part of the data package. The laboratory is required to maintain this raw data in an orderly manner and to have these records available for review by EMAP-E personnel upon request (i.e., the data may be audited at any time following appropriate notification of the laboratory). The first-step validation checks performed by Province personnel will be limited to the following: 1.) a check to verify that all reporting units and numbers of significant figures are correct; 2.) a check to verify that all of the laboratory's calculated percent recovery values (for calibration check samples, Laboratory Control Materials, and matrix spikes) and relative percent difference values (for duplicates) are correct; and 3.) a check to verify that the reported concentrations for each analyte fall within "environmentally-realistic" ranges, determined from previous studies and expert judgement. In addition,

past studies indicate that the different compounds in each class of chemicals being measured on EMAP-E (e.g., PAHs, PCBs, DDTs and other chlorinated pesticides) typically occur in the environment in somewhat fixed ratios to one another. For example, the DDT breakdown products p,p DDD and p,p DDE typically can be expected to occur at higher concentrations than p,p DDT in estuarine sediments of the East Coast. If anomolous departures from such expected ratios are found, it may indicate a problem in the measurement or data reduction process requiring further investigation.

The second major aspect of data validation is to compare the QA/QC data against established criteria for acceptable performance, as specified earlier in this plan. This will involve the following specific steps:

1.) Results for QA/QC samples should be tabulated, summarized and evaluated. Specifically, a set of summary tables should be prepared from the Province database showing the percent recovery values and relative percent difference values (where applicable) for the following QA/QC samples: continuing calibration checks samples, laboratory control material(s), and matrix spike/matrix spike duplicate samples. The tables should indicate the percent recovery values for these samples for each individual batch of samples, as well as the average, standard deviation, coefficient of variation, and range for all batches combined.

2.) Similar summary tables should be prepared for the laboratory reagent blank QA/QC samples.

3.) The summary results, particularly those for the Laboratory Control Material (i.e., Certified Reference Material), should be evaluated by comparing them against the QA/QC warning and control limit criteria for accuracy, precision, and blank contamination specified in Table 5-4.

4.) Method detection limits reported by the laboratory for each analyte should be tabulated and compared against the target values in Table 5-5.

There are several possible courses of action to be taken if the reported data are found to be deficient (i.e., warning and/or control limits exceeded) during the assessment of data quality:

1.) The laboratory's cover letter (narrative explanation) should be consulted to determine if the problems were satisfactorily addressed.

2.) If only warning limits were exceeded, then it is appropriate for the laboratory to report the results. Exceedance of control limits, however, will result in one of the following courses of action: 1.) all associated results will be qualified in the database as estimated values (as explained in the following section), or 2.) the data will be rejected and deleted from the database because the analysis was judged to be out of control (based on the professional judgement of the reviewer). Rejection of data due to failure of the laboratory's quality control system could ultimately result in disqualification of the laboratory from further participation in the EMAP-Estuaries program.

Assigning Data Qualifier Codes

Data qualifier codes are notations used by laboratories and data reviewers to briefly describe, or qualify, data and the systems producing data. As previously indicated, EMAP-E laboratories are expected to assign only two data qualifier codes ("a" and "b") to data values before submitting them to the program. EMAP-E data reviewers, in turn, will assign an additional data qualifier code in situations where there are exceedances of control limit criteria. The most typical situation is when a laboratory fails to meet the accuracy control limit criteria for a particular analyte in a Certified Reference Material or matrix spike sample. In these situations, the QA reviewer should verify that the laboratory did meet the control limit criteria for precision. If the lack of accuracy is found to be consistent (i.e., control limit criteria for precision were met), then it is likely that the laboratory experienced a true bias for that particular analyte. In these situations, all reported values for that particular analyte will be qualified with a "c" code. The "c" code has the following meaning: "The reported concentration is considered an estimate because control limits for this analyte were exceeded in one or more quality control samples."

Because some degree of expert judgement and subjectivity typically is necessary to evaluate chemistry QA/QC results and assign data qualifier codes, data validation should be conducted only by qualified personnel. It is the philosophy of the program that data which are qualified as estimates because of minor exceedance of a control limit in a QA/QC sample ("c" code) are still usable for most assessment and reporting purposes. However, it is important

to note that all QA/QC data will be readily available in the database along with the results data, so that interested data users can make their own estimation of data quality.

Taking Final Action

Upon completion of the above steps, a report summarizing the QA review of the data package should be prepared, samples should be properly stored or disposed of, and laboratory data and accompanying explanatory narratives should be archived both in a storage file and in the database. Technical interpretation of the data begins after the QA review has been completed.

Reports documenting the results of the QA review of a data package should summarize all conclusions concerning data acceptability and should note significant quality assurance problems that were found. These reports are useful in providing data users with a written record on data concerns and a documented rationale for why certain data were accepted as estimates or were rejected. The following specific items should be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.
- Brief descriptions of analytical methods and the method(s) used to determine detection limits.
- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.
- Descriptions of initial and ongoing calibration results, blank contamination, and precision and bias relative to QA plan objectives (including tabulated summary results for Certified Reference Materials and matrix spike/matrix spike duplicates).

The chemistry QA results will be presented in the Program Annual Quality Assurance Report and will also become a permanent part of the database documentation (i.e., metadata). The QA/QC data collected by the Program will be used not only to assess the accuracy and precision of individual laboratory measurements, but ultimately to assess the comparability of data generated by multiple laboratories.

SECTION 6

SEDIMENT PARTICLE SIZE ANALYSIS

6.1 OVERVIEW

Particle size is used to characterize the physical characteristics of sediments. Because particle size influences both chemical and biological variables, it can be used to normalize chemical concentrations according to sediment characteristics and to account for some of the variability found in biological assemblages. For 1993 EMAP-E monitoring in the Virginian Province, only the percent silt-clay will be determined for the particle size samples.

6.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING

EMAP-E protocols for collecting particle size samples are described in detail in the Virginian Province Field Operations and Safety Manual (Reifsteck et al. 1993). Samples will be collected in plastic Whirl-pak® containers; a minimum sample size of 100 grams is recommended. Samples should be held and shipped on ice (NOT dry ice) and may be stored at 4 °C for up to one year before analysis. Samples must not be frozen or dried prior to analysis, as either process may change the particle size distribution.

6.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

Quality control of sediment particle size analysis is accomplished by strict adherence to protocol and documentation of quality control checks. Certain procedures are critical to the collection of high quality data. For example, it is essential that each sample be homogenized thoroughly in the laboratory before a subsample is taken for analysis. Laboratory homogenization should be conducted even if samples were homogenized in the field. Furthermore, all screens used for dry seiving must be clean before conducting analysis, and all of the sample must be retrieved from them. To clean a screen, it should be inverted and tapped on a table, while making sure that the rim hits the table evenly. Further cleaning of brass screens may be performed by gentle scrubbing with a stiff bristle nylon brush. Stainless steel screens may be cleaned with a nylon or brass brush.

The most critical aspect of the pipet analysis is knowledge of the temperature of the silt-clay suspension. An increase of only 1 °C will increase the settling velocity of a particle 50 µm in diameter by 2.3 percent. It is generally recommended that the pipet analysis be conducted at a constant temperature of 20 °C. However, Plumb (1981) provides a table to correct for settling velocities at other temperatures; this table is included in the EMAP-E Laboratory Methods Manual (U.S. EPA, in preparation). If the mass of sediment used for pipet analysis exceeds 25 g, a subsample should be taken as described by Plumb (1981). Silt-clay samples in excess of 25 g may give erroneous results because of electrostatic interactions between the particles. Silt-clay samples less than 5 g yield a large experimental error in weighing relative to the total sample weight. Thorough mixing of the silt-clay suspension at the beginning of the analysis also is critical. A perforated, plexiglass disc plunger is very effective for this purpose. Once the pipet analysis begins, the settling cylinders must not be disturbed, as this will alter particle settling velocities. Care must be taken to disturb the sample as little as possible when pipet extractions are made.

The analytical balance, drying oven, sieve shaker, and temperature bath used in the analysis should be calibrated at least monthly. Dried samples should be cooled in a dessicator and held there until they are weighed. If a dessicator is not used, the sediment will accumulate ambient moisture and the sample weight will be overestimated. A color-indicating desiccant is recommended so that spent desiccant can be detected easily. Also, the seal on the dessicator should be checked periodically, and, if necessary, the ground glass rims should be greased or the "O" rings should be replaced.

Quality control for the sediment analysis procedures will be accomplished primarily by reanalyzing a randomly selected subset of samples from each batch, as described in full detail in the EMAP-E Laboratory Methods Manual (U.S. EPA, in preparation). A batch of samples is defined as a set of samples of a single textural classification (*e.g.*, silt/clay, sand, gravel) processed by a single technician using a single procedure. Approximately 10% of each batch completed by the same technician should be reanalyzed (*i.e.*, reprocessed) in the same manner as the original sample batch. Based on results typically attained by experienced technicians, if the absolute difference between the original value and the second value is greater than 10% (in terms of the percent of the most abundant sediment size class), then a third analysis will be completed by a different technician. The values closest to the third value will be entered into the database. In addition, all the other samples in the same batch must be re-analyzed, and the laboratory protocol

and/or technician's practices should be reviewed and corrected to bring the measurement error under control. If the percent of the most abundant sediment size class in the original sample and the reanalyzed sample differs by less than 10, the original value will not be changed and the sediment analysis process will be considered in control.

Additional quality control for particle size analyses will be accomplished by reanalyzing samples that fail either a range check or recovery check. For the range check, any sample results that fall outside expected ranges (i.e., any percentage that totals greater than 100%) will be reanalyzed. For the recovery check, if the total weight of the recovered sands is 10% (by weight) less or greater than the starting weight of sands, the sample must be reanalyzed.

6.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

6.4.1 Sample Tracking

EMAP-E information management personnel have developed a comprehensive system for barcode labeling of sample containers, recording sampling information in the field and tracking sample shipments. A complete description of this system is provided in the EMAP-E Information Management Plan (Adams et al. 1993) and also summarized in Section 11 of this plan. The laboratory responsible for processing the sediment particle size samples must designate a sample custodian, authorized to check the condition of and sign for the incoming field samples, obtain documents of shipment and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the Province Information Management center. The use of barcode labels and readers provided by the Province will facilitate this process. Laboratory personnel should be aware of the required sample holding times and conditions for particle size samples, and there must be clearly-defined custody procedures for sample handling, storage, and disbursement in the laboratory.

6.4.2 Data Reporting Requirements and Evaluation Procedures

The weight of each sediment fraction should be reported to the nearest 0.0001 gram dry weight. The laboratory should report the results for all samples analyzed (including QC duplicates) both in hard copy and in a computer-readable format specified by the Province Information Manager. In addition, both the paper and electronic

data packages should include a cover letter with a summary of all quality control checks performed and a narrative explanation of any problems that may have influenced data quality.

It is the responsibility of the Province Manager to acknowledge initial receipt of the data package(s), verify that the four data evaluation steps identified in the following paragraph are completed, notify the laboratory of any additional information or corrective actions deemed necessary as a result of the Province's data evaluation and, following satisficatory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for the Province Manager to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. It is the responsibility of the Province QA Coordinator to closely monitor and formally document each step in the data evaluation process as it is completed. This documentation should be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist should be supplemented with detailed memos to the electronic and paper project files outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package should commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten and (if holding times have been exceeded) can sometimes limit options for reanalysis. The first part of data evaluation is to verify that all required information has been provided in the data package. On the EMAP-E program, this should include the following specific steps:

- Province personnel should verify that the package contains a cover letter signed by the laboratory manager, hard copies of all results (including QA/QC results), and accompanying computer diskettes.

- The electronic data file(s) should be parsed and entered into the EMAP Province database to verify that the correct format has been supplied.

- Once the data have been transferred to the Province database, automated checks should be run to verify that results have been reported for all expected samples and all analytes.

The Province Manager should contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory should provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Data validation, or the process of assessing data quality, should begin after Province personnel have determined that the data package is complete. Data validation for particle size data should consist of the following: 1.) a check to verify that all reporting units and numbers of significant figures are correct; 2.) a check to verify that the cumulative percentage of each particle size fraction never exceeds 100% (i.e., a failed range check); 3.) a check to verify that the results for duplicate samples do not differ by more than 10%; and 4.) the relative standard deviation (RSD) for the three particle size samples obtained at each station should be calculated. For any station having an RSD greater than 20%, all raw data and calculations should be checked by the laboratory to ascertain that the difference truly reflects natural spatial variability among the three grab samples and not measurement error.

6.4.3 Assigning Data Qualifier Codes and Taking Final Action

Data qualifier codes are notations used by laboratories and data reviewers to briefly describe, or qualify, data and the systems producing data. To date, the Virginian Province particle size data has been accepted without qualification, and no data qualifier codes have been developed. All QA/QC data associated with particle size analyses will be readily available in the database along with the results data, so that interested data users can perform their own assessments of data quality.

Upon completion of all data evaluation steps, a report summarizing the QA review of the data package should be prepared, samples should be properly stored or disposed of, and laboratory data should be archived both in a storage file and in the database. Reports documenting the results of the QA review of the data package should summarize all conclusions concerning data acceptability and should note significant quality assurance problems that were found. These reports are useful in providing data users with a written record of data concerns and a documented rationale for why certain data were accepted as estimates or were rejected. The following specific items should be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.

- Brief descriptions of sample collection and analysis methods.

- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.

The particle size QA results will be included in the annual Program Quality Assurance Report and will also become a permanent part of the database documentation (i.e., metadata).

SECTION 7

SEDIMENT TOXICITY TESTING

7.1 OVERVIEW

The toxicity of sediments collected by field crews will be determined as an integral part of the benthic indicator suite, using 10-day acute toxicity tests with the marine amphipod *Ampelisca abdita*. The various aspects of the test for which QA/QC procedures are specified in this section include the following: sample collection, preservation and holding, the condition of testing facilities and equipment, the source and condition of test organisms, test conditions, instrument calibration, use of reference toxicants, record keeping, data reporting requirements and data evaluation. In addition, any laboratory which has not previously performed the sediment toxicity test using *Ampelisca abdita* will be required to perform an initial demonstration of capability, as described below.

7.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING

Protocols for sample collection, preservation and holding are presented in the Field Operations and Safety Manual (Reifsteck *et al*. 1993). Sediment samples for toxicity testing should be chilled to 4 °C when collected, shipped on ice, and stored in the dark at 4 °C until used. The minimum volume of sediment required per station is 3000 ml (i.e., 3 liters). The sediment should be stored for no longer than four weeks before the initiation of the test and should not be frozen or allowed to dry. Sample containers should be made of chemically inert materials (e.g., glass or high density polyethylene jars with Teflon® lined lids) to prevent contamination, which might result in artificial changes in toxicity.

Sediment for toxicity testing is taken from the same homogenate used for the sediment chemistry sample; this homogenate consists of the top 2 cm layer (approximate) taken from multiple grabs at each station. As with the sediment chemistry sample, contamination is to be avoided in obtaining the sediment toxicity sample. This is accomplished through strict adherence to protocol during sample collection. For example, all sampling devices and any other instruments in contact with the sediment should be cleaned with water and a mild detergent and thoroughly

rinsed between stations, and all utensils in contact with the sample should be made of chemically inert materials, such as Teflon® or high quality stainless steel (see Reifsteck *et al*. 1993).

7.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

Complete descriptions of the methods employed for the sediment toxicity test are provided in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision); these protocols are based on American Society for Testing and Materials (ASTM) Standard Methods (ASTM 1991).

7.3.1 Facilities and Equipment

Laboratory and bioassay temperature control equipment must be adequate to maintain recommended test temperatures. Recommended materials must be used in the fabrication of the test equipment in contact with the water or sediment being tested, as specified in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision).

7.3.2 Initial Demonstration of Capability

Laboratories which have not previously conducted sediment toxicity tests with *Ampelisca abdita* must demonstrate the ability to collect (if applicable), hold and test the organisms without significant loss or mortality, prior to initiating testing of actual samples. There are two types of tests which must be performed as an initial demonstration of capability; these tests will serve to indicate the overall ability of laboratory personnel to handle the organism adequately and obtain consistent, precise results. First, the laboratory must perform a minimum of five successive reference toxicant tests, using sodium dodecyl sulfate (SDS) as the reference toxicant. For *Ampelisca abdita*, short-term (*i.e*., 96-hour) tests without sediments (*i.e*., seawater only) can be used for this purpose.

The trimmed Spearman-Karber method of regression analysis (Hamilton *et al*. 1977) or the monotonic regression analysis developed by DeGraeve *et al*. (1988) can be used to determine an LC50 value for each 96-hour reference toxicant test. The LC50 values should be recorded on a control chart maintained in the laboratory (as described previously in section 3.2.5 of this document). Precision then can be described by the LC50 mean, standard

deviation, and percent relative standard deviation (coefficient of variation, or CV) of the five (or more) replicate reference toxicant tests. If the laboratory fails to achieve an acceptable level of precision in the five preliminary reference toxicant tests, the test procedure should be examined for defects and the appropriate corrective actions should be taken. Precision is considered acceptable when the LC50 values for five consecutive reference toxicant tests fall within the 95% confidence interval warning limits on the control chart. Additional tests should be performed until acceptable precision is demonstrated.

The second series of tests which must be performed successfully prior to the testing of actual samples are 10-day, "non-toxicant" exposures of *Ampelisca abdita*, in which test chambers contain the control sediment and seawater that will be used under actual testing conditions. These "control" tests should be performed concurrent with the reference toxicant tests used to assess single laboratory precision. At least five replicate test chambers should be used in each test. The tests should be run in succession until two consecutive tests each have mean survival equal to or greater than 85% and survival in the individual test chambers is not less than 80%. These are the control survival rates which must be achieved during actual testing if a test is to be considered acceptable (ASTM 1991; see section 7.3.5); therefore, the results of this preliminary demonstration will provide evidence that facilities, water, control sediment, and handling techniques are adequate to result in successful testing of samples. The testing facility is required to submit the results of the initial demonstration of performance to the Province Manager and receive written approval to initiate testing of actual samples.

7.3.3 Quality of Test Organisms

Amphipods used in the tests should appear to be healthy (i.e., active with full guts) and should be positively identified to species by a qualified individual. If the amphipods are collected from the field prior to testing, they should be obtained from an area known to be free of toxicants and should be held in clean, uncontaminated water and facilities. Amphipods held prior to testing should be checked daily, and individuals which appear unhealthy or dead should be discarded. If greater than 5% of the organisms in holding containers are dead or appear unhealthy during the 48 hours preceding a test, the entire group should be discarded and not used in the test.

Test organisms should be as uniform as possible in age and size. For EMAP-E sediment toxicity testing, juvenile *Ampelisca abdita* in the size range 2 to 4 mm should be used for testing. Only active, apparently healthy individuals should be selected for testing; care should be taken not to select gravid females or males nearing sexual maturity. To verify that the individuals used are of the appropriate size, at least one additional group of 20 to 30 amphipods must be sorted at random at the beginning of each test. This extra group should be preserved in 5% buffered formalin or 70% ethanol for later length measurement. The length of each individual in the group should be determined using a dissecting microscope and measuring from the base of the first antennae to the base of the telson. The mean, standard deviation, and range of these length measurements should be used by laboratory personnel to verify that correctly-sized individuals are being used in the tests; the length measurement data also should be reported along with the results for each test.

The sensitivity of each batch of organisms obtained for testing must be evaluated with the reference toxicant sodium dodecyl sulfate (SDS) in a short-term toxicity test performed concurrently with the sediment toxicity tests. The use of SDS as the reference toxicant is required as a means of standardizing test results among different laboratories. For *Ampelisca abdita*, a 96-hour reference toxicant test without sediment is used to generate LC50 values, as previously described in section 7.3.2.

These LC50 values should be recorded on the same control chart used to record the results of the five (or more) reference toxicant tests performed for the initial demonstration of capability. The control chart represents a "running plot" of the toxicity values (LC50s) from successive reference toxicant tests. The mean LC50 and the upper and lower warning and control limits (95% and 99% confidence interval around the mean, respectively) are recalculated with each successive point until the statistics stabilize. Outliers, which are values which fall outside the upper and lower control limits, are readily identified. The plotted values are used both to evaluate trends in organism sensitivity and to verify the overall ability of laboratory personnel to obtain consistent results.

Reference toxicant test LC50 values which fall outside control chart limits should serve as a warning to laboratory personnel. At the P=0.05 probability level, one in twenty tests would be expected to fall outside warning limits by chance only. The laboratory should try to determine the cause of the outlying LC50 value, but a retest of the samples is not necessarily required. If the reference toxicant test results are outside control chart limits on the next consecutive test, the sensitivity of the organisms and the overall credibility of the test are suspect. The test procedure

again should be examined for defects and additional reference toxicant tests performed. Testing of samples should not resume until acceptable reference toxicant results can be obtained; this may require the use of a different batch of test organisms.

7.3.4 Test Conditions

Parameters such as water temperature, salinity (conductivity), dissolved oxygen, and pH should be checked as required for each test and maintained within specified limits (U.S. EPA 1992, in revision). Instruments used for routine measurements must be calibrated and standardized according to instrument manufacturer's procedures. All routine chemical and physical analyses must include established quality assurance practices as outlined in Agency methods manuals (U.S. EPA 1979a and b) and SOP's based upon them.

Overlying water must meet the requirements for uniform quality specified in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision). The minimum requirement for acceptable overlying water is that it allows acceptable control survival without signs of organism disease or apparent stress (*i.e.*, unusual behavior or changes in appearance). The overlying water used in the sediment toxicity tests with *Ampelisca* should have a salinity of 30 ‰ and may be natural seawater, diluted hypersaline brine prepared from natural seawater, or artificial seawater prepared from sea salts. If natural seawater is used, it should be obtained from an uncontaminated area known to support a healthy, reproducing population of the test organism or a comparably sensitive species.

7.3.5 Test Acceptability

Survival of organisms in control treatments should be assessed during each test as an indication of both the validity of the test and the overall health of the test organism population. The amphipod tests with *Ampelisca abdita* are acceptable if mean control survival is greater than or equal to 85 percent, and if survival in individual control test chambers exceeds 80 percent. If these control survival rates are not achieved, the test must be re-run. Additional guidelines for acceptability of individual sediment toxicity tests are presented in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision). An individual test may be conditionally acceptable if temperature, dissolved

oxygen (DO), and other specified conditions fall outside specifications, depending on the degree of the departure and the objectives of the tests. Any deviations from test specifications must be noted in a cover letter when reporting the data so that a determination can be made of test acceptability by the Virginian Province Manager.

7.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

7.4.1 Sample Tracking

EMAP-E information management personnel have developed a comprehensive system for barcode labeling of sample containers, recording sampling information in the field and tracking sample shipments. A complete description of this system is provided in the EMAP-E Information Management Plan (Adams et al. 1993) and also is summarized in Section 11 of this plan. The laboratory responsible for performing the sediment toxicity tests must designate a sample custodian, authorized to check the condition of and sign for the incoming field samples, obtain documents of shipment and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the Province Information Management center. The use of barcode labels and readers provided by the Province will facilitate this process. Laboratory personnel must adhere to the required sample holding times and conditions for sediment toxicity samples, and there must be clearly-defined custody procedures to establish and document sample handling, storage, and disbursement in the laboratory.

7.4.2 Record Keeping and Data Reporting Requirements

It is mandatory for the toxicity testing facility to maintain thorough and complete records. Bound notebooks must be used to maintain records of the test organisms such as species, source, age, date of collection and/or receipt, and other pertinent information relating to their history and health, and information on the calibration of equipment and instruments, test conditions employed, size of organisms used in the test and test results. Signed annotations should be made on a real-time basis to prevent loss of information.

Laboratory personnel should verify that all specified QA/QC requirements are met for a given test, or, if not, that specified corrective actions are implemented and problems resolved, before proceeding with subsequent tests. In

addition, each laboratory must establish a system for detecting and eliminating transcription or calculation errors and assigning data qualifier codes prior to reporting data. It is recommended that an individual not involved directly in sample processing be designated as laboratory QA Officer to perform these verification checks independent of day-to-day laboratory operations.

The laboratory should submit only data which either have met all QA requirements or have been qualified properly using designated QA codes. Samples will be retested whenever QA requirements have not been met, and only the results of the retesting (meeting QA requirements) should be submitted. The laboratory should report the results for all successfully-tested samples both in hard copy and in a computer-readable format specified by the Province Information Manager. At a minimum, the following information should be included:

- EMAP sample ID, laboratory sample ID (if applicable), laboratory test number (allows EMAP to identify all field samples and associated controls comprising a single test), organism percent mortality for each replicate, mean percent mortality for each sample, and results of the significance test for toxicity (t-test of each sample versus the control).

- Data for all water quality measurements made during testing (i.e., dissolved oxygen, temperature, salinity, and pH) and for all QA/QC variables, such as tabulated reference toxicant test results and associated control charts and the mean, standard deviation, and range in length of the organisms, should be submitted by the laboratory along with the test results.

- Both the hard copy and electronic data packages include a cover letter with a summary of all quality control checks performed and a narrative explanation of any problems that may have influenced data quality.

7.4.3 Data Evaluation Procedures

It is the responsibility of the Province Manager to acknowledge initial receipt of the data package(s), verify that the data evaluation procedures identified in the following paragraphs are completed, notify the laboratory of any additional information or corrective actions deemed necessary as a result of the Province's data evaluation and, following satisficatory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing

that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for the Province Manager to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. It is the responsibility of the Province QA Coordinator to monitor closely and formally document each step in the data evaluation process as it is completed. This documentation should be in the form of a data evaluation tracking form or checklist that is updated as each step is completed. This checklist should be supplemented with detailed memos to both the paper and electronic project file outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package should commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten and (if holding times have been exceeded) can sometimes limit options for reanalysis. The first part of data evaluation is to verify that all required information has been provided in the data package. First, Province personnel should verify that the package contains the following: a cover letter signed by the laboratory manager, hard copies of all results (including copies of control charts and other QA/QC results), and accompanying computer diskettes. Second, the electronic data file(s) should be parsed and entered into the EMAP Province database (SAS datasets) to verify that the correct format has been supplied. Third, once the data has been transferred to the Province database, automated checks should be run to verify that results have been reported for all expected samples and that no errors occurred in converting the data into SAS datasets. This can be accomplished by visual comparision of SAS printouts and frequency distributions versus printouts of the original data supplied by the laboratory. The printouts should be used to re-verify the completeness of the data sets and to verify that values reported for all variables are correct.

The Province Manager should contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory should provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Data validation, or the process of assessing data quality, should begin after Province personnel have determined that the data package is complete. Data validation for sediment toxicity testing data should consist of the following:

- A random check of 20% of the reported results to verify that the statistical test of significance (t-test) was performed without error by the laboratory. If no errors are found, it can be assumed that this test was applied correctly to all results and no further action is necessary. If one or more errors are found, the significance tests for the entire data set must be recalculated and a request made to the laboratory for a written explanation of the error(s) and a corrective action plan

- A review of the water quality data submitted as part of the data package to verify that all specified test conditions were met.

- The QA/QC data submitted as part of the data package should be reviewed to verify that specified limits for control survival and/or reference toxicant test LC50 values were not exceeded, or, if exceeded, that the proper data qualifier codes were assigned by the laboratory (explained in the following section).

7.4.4 Assigning Data Qualifier Codes

Data qualifier codes are notations used by laboratories and data reviewers to evaluate, describe, or qualify, data and the systems producing data. To date, EMAP-E has developed a limited list of data qualifier codes which are allowed in situations where the laboratory either experienced an exceedance of a quality control limit or there was a minor deviation from the required test design or test conditions. Normally, when control limits are exceeded the laboratory is required to repeat the test for the samples in question. However, limitations on the amount of sample collected sometimes prevent retesting and data qualifier codes are required. Qualified data are still usable for most assessment purposes, but data users are alerted to the possible limitations on data use and can make their own judgements. The qualifier codes developed for EMAP-E sediment toxicity data are listed in Table 7-1 and explained in the following section. Personnel at the toxicity testing facility are responsble for reviewing the data and assigning all of these qualifier codes, except for the ST-L code, prior to submitting the data package to EMAP-E.

Table 7-1. Qualifier Codes for EMAP-E Sediment Toxicity Data.

Code	Description
ST-C	Fewer than 5 replicates were tested
ST-D	Mean control survival less than 85%
ST-E	Sample held for longer than 30 days prior to testing
ST-G	No reference toxicant test was run
ST-H	Hardness and alkalinity not measured (Virginian Province 1990 only)
ST-I	Control survival in one replicate was less than 80%
ST-J	Physical parameters out of bounds
ST-K	Less than 20 animals used per replicate
ST-L	Not used in Province Assessment

The ST-C code is assigned to the results for a given sample whenever the laboratory must use fewer than the required 5 replicates for that sample in a test. This usually occurs for a limited number of samples where an insufficient amount of sediment has been collected for testing. At a minimum, three replicates must be used for a sample's results to be considered valid, as this will still allow the laboratory to perform the statistical test for significance at test completion. Results flagged with the ST-C code will be used for EMAP-E assessments.

The ST-D code is assigned to the results for all samples from a given test when the mean survival in the test control was less than the required 85%. Normally, this invalidates the results for the test and a re-test is required, but the ST-D code is assigned when re-testing cannot be performed because there is insufficient sample remaining or sample holding times have been grossly exceeded. Results flagged with the ST-D code typically are not used for EMAP-E assessments and are of limited value.

The ST-G code is assigned to all samples from a test in which the laboratory failed to conduct the associated 48-hr, water-only reference toxicant test, as required. The reference toxicant test represents an important "positive" control which is used to assess both laboratory performance and the relative sensitivity of the test organisms. Failure to conduct this test represents an omission that does not necessarily invalidate the test results, but will necessitate closer scrutiny of the laboratory's control charts of the reference toxicant test results and a review of procedures. This check

will be done to verify that all reference toxicant tests which were performed had results within required control chart limits. Results flagged with the ST-G code typically will be used for EMAP-E assessments.

The ST-H code is assigned to certain results from the freshwater amphipod tests conducted as part of the Virginian Province 1990 Demonstration Project. The code indicates that the laboratory failed to measure hardness and alkalinity in the test chambers, as required. This does not necessarily invalidate the test, and results flagged with this code have been used for EMAP-E assessments in the past. The freshwater amphipod test was only used in 1990 and is no longer conducted in the program.

The ST-I code is assigned to all results from a test in which survival in one of the control replicates was less than the required 80%. The laboratory normally is required to repeat the test whenever this occurs, but this may not always be possible. If the mean control survival in the test was greater than 85%, then the data are used by EMAP-E for assessment purposes, but data users should be aware that all QA/QC requirements for control survival were not met.

The ST-J code is allowed in a limited number of situations where there was minor exceedance of a required control limit for one of the physical parameters measured in each test (e.g., dissolved oxygen, temperature, salinity, or pH). Minor exceedances typically do not invalidate the test results, but the laboratory must provide a written explanation of the nature and extent of the exceedance. Based on this explanation, the Province Manager, in consultation with the Province QA Officer or others, will make the final decision to allow or disallow this code assignment. The laboratory may be required to repeat the test in certain instances. Results qualified with this code are used for EMAP-E assessments.

The ST-K code is assigned to the results for any sample where the laboratory failed to use the required 20 animals per test chamber. This can occur when the laboratory failed to collect or receive from a supplier an adequate number of organisms to conduct a given test. In these instances, it is preferable to conduct the test with a fewer number of organisms in each test chamber than to use organisms which are unhealthy or outside the acceptable size (age) range. Results from tests in which fewer than 20 organisms were used per replicate typically are usable for most assessment purposes.

The ST-L code is assigned to results which are not acceptable for use in Province assessments (e.g., Annual

Statistical Reports or Assessment Reports). Typically, results from tests in which mean control survival was less than the required 85% (ST-D code) are considered invalid and are not used for assessment purposes.

7.4.5 Data Quality Reports

All QA/QC data and interpretive commentary associated with EMAP-E sediment toxicity testing will be readily available in the database along with the results data, so that interested data users can perform their own assessment of data usability. Upon completion of all data evaluation steps, a report summarizing the QA review of the data package should be prepared, samples should be properly stored or disposed of, and laboratory data should be archived both in a storage file and in the database. Reports documenting the results of the review of the data package should summarize all conclusions concerning data acceptability and should note significant quality assurance problems that were found. These reports are useful in providing data users with a written explanation of why certain data qualifier codes were assigned and/or why some data were rejected. The following specific items should be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.
- Brief descriptions of sample collection and testing methods.
- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.

The sediment toxicity testing QA reports will be included in the Program Quality Assurance Report and will also become a permanent part of the database documentation (i.e., metadata).

SECTION 8

MACROBENTHIC COMMUNITY ASSESSMENT

8.1 OVERVIEW

This section presents EMAP-Virginian Province QA/QC protocols and requirements for macrobenthic community assessment, from sample collection and laboratory analysis to validation of the resultant data and construction of a benthic index. Replicate benthic samples are obtained at each station, representing the contents of different individual grab samples. Each sample is processed individually in the laboratory to obtain an accurate assessment of the number of individuals of each species present and their biomass (i.e., weight). This information is then aggregated in various ways to construct a benthic index to discriminate between degraded and undegraded estuarine conditions.

8.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING

Sediment samples for macrobenthic community assessments will be collected at each station using a Young-modified Van Veen grab sampler. In order to be considered acceptable, each grab sample must be obtained following the protocols specified in the Virginian Province Field Operations and Safety Manual (Reifsteck *et al*. 1993). In particular, field personnel should be thoroughly trained in the proper techniques for sieving and sample preservation (using a stained and buffered formalin solution). In addition, each sediment sample must be inspected carefully before being accepted for benthic community assessment. Each of the following acceptability criteria must be satisfied (from U. S. EPA 1991):

- Sediment should not be extruded from the upper face of the sampler such that organisms may be lost.
- Overlying water should be present (indicates minimal leakage)
- The sediment surface should be relatively flat (indicates minimal disturbance or winnowing)
- The entire surface of the sample should be included in the sampler
- The grab sampler must have penetrated the sediment to a minimum depth of 7 cm

If a grab sample does not meet any one of these criteria, it should be rejected.

In the laboratory, stored samples must be easily retrieved and protected from environmental extremes. Samples cannot be allowed to freeze and should be stored above 5 °C to prevent the formation of paraformaldehyde. Temperatures greater than 30 °C should be avoided so as to retard evaporative losses. Stored and archived samples should be checked once every three months for excessive evaporative losses due to loosely-fitting or cracked container lids, or inadequately sealed jars. Exposure to direct sunlight should be minimized since long-term exposure can degrade the vital stain rose bengal.

8.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

In the laboratory, QA/QC involves a series of check systems for organism sorting, counting and taxonomic identification. These checks are described briefly in the following sections; more complete details can be found in the EMAP-E Laboratory Methods Manual (U.S. EPA, in preparation).

8.3.1 Sorting

The quality control check on each technician's efficiency at sorting (*i.e.*, separating organisms from sediment and debris) consists of an independent resort by a second, experienced sorter. A minimum of 10% of all samples sorted by each technician must be resorted (i.e., the sediment and debris remaining after the original sort is completely re-examined) to monitor performance and thus provide feedback necessary to maintain acceptable standards. These resorts should be conducted on a regular basis on at least one sample chosen at random from each batch of 10 samples processed by a given sorter. Inexperienced sorters require a more intensive QC check system. It is recommended that experienced sorters or taxonomists check each sample processed by inexperienced sorters until proficiency in organism extraction is demonstrated. Once proficiency has been demonstrated, the checks may be performed at the required frequency of one every ten samples. Bound laboratory logbooks must be maintained and used to record the number of samples processed by each technician, as well as the results of all sample re-sorts.

For each sample that is resorted, percent sorting efficiency should be calculated using the following formula:

$$\frac{\text{\# of organisms originally sorted}}{\text{\# of organisms originally sorted + additional \# found in resort}} \times 100$$

The results of sample resorts may require that certain actions be taken for specific technicians. If sorting efficiency is greater than 95%, no action is required. If sorting efficiency is between 90% and 95%, problem areas should be identified and the technician should be re-trained. Laboratory supervisors must be particularly sensitive to systematic errors (*e.g.*, consistent failure to extract specific taxonomic groups) which may suggest the need for further training. Sorting efficiencies below 90% will require resorting and recounting of all samples in the associated batch and continuous monitoring of that technician to improve efficiency.

If sorting efficiency is less than 90%, organisms found in the resort should be added to the original data sheet and, if possible, to the appropriate vials for biomass determination. If sorting efficiency is 90% or greater, the QC results should be recorded in the appropriate logbook, but the animals should be kept separate from the original sample and not used for biomass determinations. Once all quality control criteria associated with the sample resort have been met, the sample residue (e.g., sediment and debris) may be discarded.

8.3.2 Species Identification and Enumeration

Only senior taxonomists are qualified to perform re-identification quality control checks. A minimum of 10% of all samples (*i.e.*, one sample chosen at random out of every batch of ten samples) processed by each taxonomic technician must be checked by a second qualified taxonomist to verify the accuracy of species identification and enumeration. This control check establishes the level of accuracy with which identification and counts are performed and offers feedback to taxonomists in the laboratory so that a high standard of performance is maintained. Samples should never be re-checked by the technician who originally processed the sample.

Ideally, each batch of ten samples processed by an individual taxonomic technician should be from a similar habitat type (*e.g.*, all oligohaline stations). The recheck of one out of the ten samples in a batch should be done periodically and in a timely manner so that subsequent processing steps (*e.g.*, biomass determinations) and data entry may proceed. As each taxon is identified and counted during the recheck, the results should be compared to the original data sheet. Discrepancies should be double-checked to be sure of correct final results. Following re-identification, specimens should be returned to the original vials and set aside for biomass determination.

When the entire sample has been re-identified and recounted, the total number of errors should be computed. The total number of errors will be based upon the number of misidentifications and miscounts. Numerically, percent accuracy will be represented in the following manner:

$$\frac{\text{Total \# of organisms in QC recount - Total number of errors}}{\text{Total \# of organisms in QC recount}} \times 100$$

where the following three types of errors are included in the total # of errors:

1.) Counting errors (for example, counting 11 individuals of a given species as 10).

2.) Identification errors (for example, identifying Species X as Species Y, where both are present)

3.) Unrecorded taxa errors (for example, not identifying Species X when it is present)

Each taxonomic technician must maintain an identification and enumeration accuracy of 90% or greater (calculated using the above formula). If results fall below this level, the entire sample batch must be re-identified and counted. If taxonomic efficiency is between 90% and 95%, the original technician should be advised and species identifications reviewed. All changes in species identification should be recorded on the original data sheet (along with the date and the initials of the person making the change) and these changes should be entered into the database. However, the numerical count for each taxonomic group should not be corrected unless the overall accuracy for the sample is below 90%. Additional details on this protocol are provided in the EMAP-E Laboratory Methods Manual (U.S. EPA, in preparation). The results of all QC rechecks of species identification and enumeration should be recorded in a timely manner in a separate logbook maintained for this purpose.

Taxonomic identifications should be consistent within a given laboratory, and with the identifications of other regional laboratories. Consistent identifications are achieved by implementing the procedures described above and by maintaining informal, but constant, interaction among the taxonomists working on each major group. As organisms are identified, a voucher specimen collection should be established. This collection should consist of representative specimens of each species identified in samples from an individual Province in a given year. For some species, it may be appropriate to include in the voucher specimen collection individuals sampled from different geographic locations within the Province. At the end of the year, the voucher specimen collection should be sent to recognized experts for verification of the laboratory's taxonomic identifications. The verified specimens should then be placed in a permanent taxonomic reference collection. Continued collection of verified species does not require additional expert verification, because the reference collection can be used to confirm the identification. In addition, the reference collection should be used to train new taxonomists. Participation of the laboratory staff in a regional taxonomic standardization program (if available) is recommended, to ensure regional consistency and accuracy of identification.

The laboratory is required to notify the Virginian Province Manager of any taxonomic identification errors discovered by outside experts, as this may necessitate database corrections. Such corrections will be made only after further consultation with the laboratory personnel and the outside expert(s) and will be supported by written documentation which clearly explains the nature of and rationale for the changes.

All specimens in the reference collection should be preserved in 70% ethanol in labeled vials that are segregated by species and sample. More than one specimen may be in each vial. The labels placed in these vials should be made of waterproof, 100-percent (at least) rag paper and filled out using a pencil. Paper with less than a 100-percent rag content or that is not waterproofed will disintegrate in the 70-percent alcohol mixture. It is important to complete these labels, because future workers may not be familiar with the project, station locations, and other details of the work in progress. In addition, the reverse side of the label should contain information about the confirmation of the identification by experts in museums or other institutions (if appropriate). To reduce evaporation of alcohol, the lids of vials and jars can be sealed with plastic tape wrapped in a clockwise direction. The species (and other taxonomic designation) should be written clearly on the outside and on an internal label. Reference specimens should be archived alphabetically within major taxonomic groups. A listing of each species name, the name and affiliation of the person who verified the identification, the location of the individual specimen in the laboratory, the status of the

sample if it has been loaned to outside experts, and references to pertinent literature should be maintained by the laboratory performing the identifications.

Reference collections are invaluable, and should be retained at the location where the identifications were performed. In no instance should this collection be destroyed. A single person should be identified as curator of the reference collection and should be responsible for its integrity. Its upkeep will require periodic checking to ensure that alcohol levels are adequate. When refilling the jars, it is advisable to use full-strength alcohol (i.e., 95 percent), because the alcohol in the 70-percent solution will tend to evaporate more rapidly than the water.

8.3.3 Biomass Measurements

Performance checks of the balance used for biomass determinations should be performed routinely using a set of standard reference weights (ASTM Class 3, NIST Class S-1, or equivalents). In addition, a minimum of 10% of all pans and crucibles in each batch processed by a given technician must be re-weighed by a second technician as a continuous monitor on performance. Samples to be reweighed should be selected randomly from the sample batch; the results of the reweigh should be compared against the original final weight recorded on the biomass data sheet. Weighing efficiency should be calculated using the following formula:

$$\frac{\text{Original final weight}}{\text{Reweighed final weight}} \times 100$$

Based on results typically obtained by experienced technicians, if weighing efficiency is between 95% and 105%, the sample has met the acceptable quality control criteria and no action is necessary. If weighing efficiency is between either 90% to 95% or 105% to 110%, the sample has met acceptable criteria, but the technician who completed the original weighing should be consulted and proper measurement practices reviewed. If the weighing efficiency is less than 90% or greater than 110%, the sample has failed the quality control criteria and all samples in the associated batch must be reweighed (following technician retraining and/or troubleshooting of laboratory equipment to determine and eliminate the source(s) of the inconsistency). Corrections to the original data sheet should only be made in those

cases where weighing efficiency is less than 90% or greater than 110%. The results of all QC reweighings should be recorded in a timely manner in a separate logbook or data sheet and maintained as part of the documentation associated with the biomass data.

8.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

8.4.1 Sample Tracking

EMAP-E information management personnel have developed a comprehensive system for barcode labeling of sample containers, recording sampling information in the field and tracking sample shipments. A complete description of this system is provided in the EMAP-E Information Management Plan (Adams et al. 1993) and also summarized in Section 11 of this plan. The laboratory responsible for processing the macrobenthic community samples must designate a sample custodian, authorized to check the condition of and sign for the incoming field samples, obtain documents of shipment and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the Province Information Management center. The use of barcode labels and readers provided by the Province will facilitate this process. In addition, the laboratory must have clearly-defined custody procedures for sample handling, storage, and disbursement in the laboratory and must maintain accurate and timely records of the location and status of all samples.

8.4.2 Record Keeping and Data Reporting Requirements

It is mandatory for the laboratory responsible for processing the macrobenthic community samples to maintain thorough and complete records. All data generated in the laboratory should be recorded directly onto standardized data forms, modeled after those presented in the EMAP Laboratory Methods Manual (U. S. EPA, in preparation). These forms are prepared for each benthic sample prior to laboratory processing and are already filled out with species names, the biomass group for each species and an 8-character code for each species consisting of the first four letters each of the genus and species names. Preparation of data sheets prior to sample processing facilitates sample tracking, sample processing, QA/QC procedures, and data entry and helps to minimize transcription and other errors. Data forms should be designed so that all necessary information is recorded clearly and unambiguously; data should be recorded in ink and signed by the responsible person. Data forms should be linked to specific samples using the bar coded

sample numbers assigned by the Province Information Management team prior to field sampling. Completed data sheets and QA/QC forms should be kept in bound notebooks arranged by type; these forms should be made available to the Province Manager upon request and will be inspected for adequacy during QA audits.

Laboratory managers should verify that all specified QA/QC requirements are met for a given batch of samples, or, if not, that specified corrective actions are implemented and problems resolved, before a technician is permitted to proceed with sample processing. The laboratory must establish a comprehensive information management system that allows responsible personnel to detect and eliminate transcription and/or calculation errors prior to submission of the final data package in computer readable format. This might include, for example, data entry procedures that involve double entry of information from the laboratory datasheets into separate databases and subsequent comparison to ensure a high level of data transcription accuracy. Data transcription errors also can be minimized through the use of computer data entry forms that duplicate or closely mirror the format of the hard copy data sheets used in the laboratory. The laboratory's manager or QA Officer should perform manual checks on a random subset of all transcribed data sheets (at least 10% of the total) to verify transciption accuracy.

The laboratory should report the results for all samples both in hard copy and in a computer-readable format specified by the Province Information Manager. At a minimum, the following information should be included: EMAP sample ID, laboratory sample ID (if applicable), numbers of individuals per sample for each species (i.e, abundance), and biomass measurements for each biomass group expressed in dry weight to the 0.1 mg. Tables summarizing the results of QC checks (e.g., resorts, recounts, reidentifications and reweighings) must be included as part of the data package, as well as a cover letter signed by the Laboratory Manager containing a narrative explanation of any problems that may have influenced data quality.

8.4.3 Data Evaluation Procedures

It is the responsibility of the Province Manager to acknowledge initial receipt of the data package(s), verify that the data evaluation procedures are completed, notify the laboratory of any additional information or corrective actions deemed necessary as a result of the Province's data evaluation and, following satisficatory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing that the submitted results have been

officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for the Province Manager to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. It is the responsibility of the Province QA Coordinator to monitor closely and formally document each step in the data evaluation process as it is completed. This documentation should be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist should be supplemented with detailed memos to the project file outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package should commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten. The first part of data evaluation is to verify that all required information has been provided in the data package. First, Province personnel should verify that the package contains the following: a cover letter in both electronic (i.e., computer text file) and paper formats (signed by the laboratory manager), hard copies of all results (including tables summarizing the results of all QA/QC checks), and accompanying computer diskettes. Second, the electronic data file(s) should be parsed into the EMAP Province database (SAS datasets) to verify that the correct format has been supplied. Third, once the data has been transferred to the Province database, automated checks should be run to verify that results have been reported for all expected samples and that no errors occurred in converting the data into SAS datasets. This can be accomplished by visual comparision of SAS printouts against printouts of the original data supplied by the laboratory. The printouts should be used to verify the completeness of the data sets and to verify that values reported for all variables are correct.

The Province Manager should contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory should provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Data validation, or the process of assessing data quality, should begin after Province personnel have determined that the data package is complete. Data validation for the benthic community assessment should consist of a thorough review of the summarized QA/QC data submitted as part of the data package to verify that specified control limits for sample resorts, species recounts and reidentifications, and biomass reweighings were not exceeded,

or, if exceeded, that specified corrective actions were implemented and are explained in adequate detail in an accompanying cover letter. If all specified control limits were met during sample processing and/or problems adequately explained, the data can be accepted for use without qualification. To date, no data qualifier codes have been needed for the Virginian Province benthic community data sets.

8.4.4 Data Quality Reports

All QA/QC data associated with the laboratory processing of benthic samples will be presented in Virginian Province reports and publications along with the results data, so that interested data users can make their own assessment of data usability. Upon completion of all data evaluation steps, a report summarizing the QA review of the data package should be prepared, samples should be properly stored or disposed of, and laboratory data and associated commentary should be archived both in a storage file and in the database. Reports documenting the results of the review of the data package should summarize all conclusions concerning data acceptability and should note significant quality assurance problems that were found. These reports are useful in providing data users with a written explanation of why certain data qualifier codes were assigned and/or why some data was rejected. The following specific items should be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.
- Brief descriptions of sample collection and testing methods.
- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.

The benthic community assessment QA data will be presented in the Quality Assurance section of the Province Annual Statistical Summary and will also become a permanent part of the database documentation (i.e., metadata).

8.5 DEVELOPMENT AND VALIDATION OF THE BENTHIC INDEX

Benthic assemblages have many attributes that make them reliable and sensitive indicators of the ecological condition of estuarine environments. Based on this supposition, the EMAP-E Program is attempting to construct a

benthic index which reliably discriminates between degraded and undegraded estuarine conditions. Construction of a benthic index and subsequent validation of the index are ongoing processes both in the Virginian and Louisianian Provinces. EMAP-E's first attempt at construction of a benthic index occurred in 1991 using benthic community abundance and biomass data collected as part of the 1990 Virginian Province Demonstration Project. Detailed descriptions of the methods used to construct the 1990 benthic index and subsequently to validate this index are provided in the 1990 Demonstration Project Report (Weisberg et al. 1993) and in a series of Virginian Province documents (Rosen 1993; U.S. EPA, in prep.). Briefly, the following major steps are followed in constructing and validating the benthic index:

1.) Degraded and undegraded (i.e., reference) stations are identified on the basis of measured near-bottom dissolved oxygen concentrations, sediment contaminant concentrations and sediment toxicity.

2.) A list of "candidate" parameters is developed using the species abundance and biomass data. This list includes metrics having ecological relevance (e.g., species diversity indices, numbers of suspension-feeding organisms, numbers of deposit-feeding organisms, etc.) that potentially might be used to discriminate between degraded and reference areas.

3.) A value for each candidate parameter is calculated for each of the previously-identified degraded and reference stations.

4.) A series of t-tests is performed to reduce the list of candidate parameters to a manageable number from which it is highly probable that a subset(s) can be identified to discriminate reliably between degraded and undegraded areas.

5.) The parameters resulting from step 4 are entered into a canonical discriminant analysis to develop a discriminant function incorporating those parameters which best discriminate degraded and reference areas. As part of this iterative process, the frequency with which reference sites are incorrectly classified as degraded (i.e., false positives), and the frequency with which degraded sites are classified as reference areas (i.e., false negatives) is calculated.

6.) The index is scaled so that values range between 1 and 10 (for ease of understanding). The mean between the highest value which reliably discriminates the degraded stations and the lowest value which reliably discriminates the reference stations is defined as the critical value. A discriminant score is then calculated for the *aprior* degraded and reference stations to determine rates of correct and incorrect classification. In addition, a cross-validation procedure is performed in which each station is removed from the calibration data set and used as a test case for validation.

7.) The index is validated using an independent data set (e.g., a different set of degraded and reference stations from the set used to construct the index) to determine rates of correct and incorrect classification (i.e., classification efficiency). If the rate of correct classification is unacceptably low (i.e., less than 80%), the

index is reconstructed and eventually re-validated beginning at the first step. The objective is to construct a benthic index which consistently results in high rates of correct classification (i.e., at least greater than 80%).

From a quality assurance perspective, there are several important issues that must be addressed in the development and application of the benthic index. These issues exist at several levels. At the most basic level, construction of the benthic index can be viewed as a multistep process involving many data manipulations (i.e., several levels of data aggregation and calculation of numerous parameters) followed by an iterative series of statistical tests. At this level, a concomitant series of independent checks must be performed to verify that each of the many data transformations and aggregations are performed without error. In addition, it is important to verify that certain data aggregations and calculations which are "generic" in nature are performed in a manner that is consistent and comparable between years and among different Provinces. Principal investigators, with the oversight of the Province QA Coordinator, are responsible for developing a system of independent checks and for confirming and documenting that they are implemented at each step in the construction of the benthic index. As a required part of this verification procedure, the personnel directly involved in constructing the index must provide, for review, detailed written documentation of each step, including documentation of computer programs that are used to manipulate data and perform calculations.

It is also essential in construction of the benthic index that there is consistency between years and among Provinces in the statistical methods employed. As part of the required series of checks prescribed above, there should be an indepedent review of these procedures by one or more qualified individuals who are not directly involved in constructing the index. There are two aspects to this review. First, there should be independent verification that the correct statistical tests are being employed. Second, there should be verification that the chosen statistical tests are being performed correctly. Again, it is the responsibility of the Province QA Coordinator to confirm and document that these independent reviews are conducted.

Another potential QA/QC concern with respect to the benthic index is the classification of different species into certain descriptive categories based on their presumed ecological niche or behavioral characteristics (e.g., "deposit feeder", "suspension feeder", "equilibrium species", "opportunistic species", etc.). This categorization is accomplished using information from the scientific literature supplemented by expert opinion. Because reliance on expert opinion introduces a certain level of subjectivity into the process of constructing a benthic index, it is important that adequate documentation be developed to justify the species classifications used at any given time. Personnel responsible for

constructing the index should enlist the help of one, or, preferably, several qualified benthic ecologists in classifying species and preparing this documentation.

On another level, a primary concern regarding the benthic index is how well it fulfills the objective of discriminating among degraded and undegraded estuarine conditions. This concern will be addressed on an continuous basis, using the cross-validation and year-to-year independent validation steps (steps 6 and 7 above) which are integral aspects of the ongoing iterative procedures involved in constructing an index. In future development of the index, additional sites will be added to the calibration data set so that it includes the full range of environmental habitats and stressors present. Furthermore, as more is learned about other measures that are effective for discriminating sites of differing environmental quality, they can be incorporated into the calibrations. The flexibility of the index development process will allow these additional selected measures to be incorporated so that eventually, a consistently high level of classification efficiency will be achieved.

SECTION 9

MEASUREMENTS OF FISH COMMUNITY STRUCTURE AND PATHOLOGY

9.1 OVERVIEW

This section presents EMAP-Virginian Province QA/QC protocols and requirements for fish community structure analyses, from sample collection and laboratory analysis to final validation of the resultant data. Collection and analysis methods are documented in the 1993 Field Operations and Safety Manual (Reifsteck *et al*. 1993). Data on species identification, enumeration, and length measurements are generated by the field crews, whereas pathology data result from laboratory analyses.

Field crews are expected to conduct a "standard" 10-minute trawl at all stations. The contents of the net are examined and fish identified to species, measured, and examined for evidence of gross external pathologies. Those fish suspected of having a pathology are preserved in a fixative and shipped to a laboratory-based pathologist for further examination.

9.2 QUALITY CONTROL PROCEDURES: FIELD OPERATIONS

9.2.1 Trawling

Fish community structure data (species identification, enumeration, and length) are significantly influenced by the collection methods. It is therefore critical that strict adherence to prescribed sampling protocols be maintained. Factors influencing the catch are gear, fishing the trawl, trawl duration, and trawl speed. All crews must be provided with "standard" nets to assure comparability of gear, and the importance of keeping the trawl duration and speed within established limits should be stressed during training. During sampling, crews must record "speed over bottom" and trawl duration on the fish trawl datasheet. In addition, the computerized data acquisition system contains a clock which automatically monitors trawl time and records the trawl duration in an electronic data file. As part of the crew

chief's daily review of the electronic data, he/she must compare all data in the electronic file with those on the hard-copy datasheets. Any discrepancies must be investigated and corrected.

Adherence to collection methodology will be monitored during initial certification of the field crew during all subsequent audits and field inspections conducted by senior Program personnel during the sampling season.

9.2.2 Species Identification, Enumeration, and Length Measurements

Fish species identification, enumeration and individual lengths must be determined in the field following protocols presented in the Virginian Province Field Operations and Safety Manual (Reifsteck *et al*. 1993). The quality of fish identifications, enumerations and length measurements are assured principally through rigorous training and certification of field personnel prior to sampling. Qualified taxonomists will provide independent confirmation of all fish identifications, enumerations and length measurements made by crew members during laboratory training sessions. Fish identifications, enumerations and length measurements also will be confirmed by the QA Coordinator, Province Manager, or their designee(s) during field visits. In addition, each field crew is required to save two "voucher" specimens of each species identified in the field. These voucher specimens should be preserved in fixative and sent back to the Field Operations Center prior to the completion of each "work shift" throughout the field season. A qualified fish taxonomist must verify the species identifications and provide immediate feedback to the field crews whenever errors are found. All erroneous identifications for a given field crew should be corrected in the database, and the crew informed of the taxonomist's findings prior to their returning to the field. Preserved voucher fish will be saved to provide a reference collection for use in subsequent years' training.

The accuracy of length measurements and individual counts will be checked during all QA audits and field visits conducted by senior Program personnel. To maintain a consistent level of field crew performance, the EMAP-E program has established an overall accuracy goal of 90% (i.e., less than 10% errors) for all fish identifications, enumerations and length measurements in a given sampling season. If this goal is not met, corrective actions will include increased emphasis on training and more rigorous testing of field crews prior to the next year's sampling season.

9.3 QUALITY CONTROL PROCEDURES: GROSS EXTERNAL PATHOLOGY AND HISTOPATHOLOGY

Fish collected in standard trawls must be examined by the field crew for evidence of gross external pathologies (lumps, growths, ulcers, and fin erosion) according to the protocols outlined in the Virginian Province Field Operations and Safety Manual (Reifsteck *et al*. 1993). As with fish identification and enumeration, the quality of gross pathology determinations can be assured principally through rigorous training and certification of field personnel prior to sampling. Qualified pathologists will be responsible for planning and overseeing all crew training for this indicator. Because of the potential difficulty in the proper identification of pathologies by inexperienced personnel, all definitive examinations will be conducted by a qualified pathologist. Field crews will be instructed to observe all fish and preserve any suspected of having one of the four pathologies listed above. These will be returned to the laboratory with a sample ID tag and the suspected pathology noted.

Upon receipt of a sample at the laboratory, the pathologist will examine these fish and provide the QA Coordinator with the results. When there is disagreement between the field observation and the pathologist's interpretation, a second pathologist will be consulted to verify the results from the primary laboratory.

Crews also will be required to preserve "pathology-free" fish collected at selected stations for examination by the pathologist to determine the potential error rate of "false negatives". Stations where these reference fish are to be collected are listed in the Field Operations and Safety Manual (Reifsteck *et al*. 1993). Fish collected for histopathological examination must be preserved according to the protocols described in the Field Operations and Safety Manual. Failure to follow these protocols will result in inadequate penetration of the fixative into the internal organs, rendering the samples useless.

A series of internal and external laboratory QC checks should be employed to provide verification of the fish histopathology identifications. In laboratories having multiple pathologists, all cases bearing significant lesions should be examined and verified by the senior pathologist. At least 5% of the slides read by one pathologist should be selected at random and read by a second pathologist without knowledge of the diagnoses made by the initial reader. For the external QC check, at least 5% of the slides should be submitted for independent diagnosis to a pathologist not involved

with the laboratory. These slides should represent the range of pathological conditions found during the study, and the external pathologist should not be aware of the diagnoses made by the laboratory personnel.

Each laboratory also should maintain a reference collection of slides that represent every type of pathological condition identified in the EMAP-E fish. Each of these slides should be verified by an external pathologist having experience with the species in question. The reference slide collection then can be used to verify the diagnoses made in future years to ensure intralaboratory consistency. The reference slides also can be compared with those of other laboratories to ensure interlaboratory consistency. A reference collection of photographs also will be made for training purposes.

9.4 QUALITY CONROL PROCEDURES: INFORMATION MANAGEMENT

9.4.1 Sample Tracking

EMAP-E information management personnel have developed a comprehensive system for barcode labeling of fish specimens, recording sampling information in the field, and tracking sample shipments. A complete description of this system is provided in the EMAP-E Information Management Plan (Adams *et al*. 1993) and is also summarized in Section 11 of this plan. Field crews must carefully and thoroughly complete all shipment datasheets and transmit this information to the Field Operations Center during the next scheduled electronic transfer of data.

Each analytical laboratory receiving fish for verification of species identifications, gross pathology or further histopathological examination must designate a sample custodian who is authorized to check the condition of and sign for the incoming samples, obtain documents of shipment, and verify sample custody records. This individual is required, upon receipt of fish samples, to record and transmit all tracking information to the Province Information Management Center. The use of barcode labels and readers provided by the Province will facilitate this process. There must be clearly-defined custody procedures for handling, storage, and disbursement of the fish samples in the laboratory.

9.4.2 Data Reporting Requirements

All field data must be entered into the field computer within one day of collection. Crew chiefs must review all data prior to electronic transfer to the Field Operations Center the following evening. Hard-copy original datasheets must be returned to the Field Operations Center no later than the end of the crew's work shift.

Following laboratory examination of the fish, only data which have met QA/QC requirements should be submitted to EMAP-E. Each data package submitted by the laboratory should consist of the following:

- A cover letter providing a brief description of the procedures and instrumentation used for verification of species identifications, gross pathology or further histopathological examination, as well as a narrative explanation of any problems encountered or failure(s) to meet required quality control limits. A copy of the cover letter in electronic format (i.e., computer-readable text file) must also be submitted.
- Tabulated results in hard-copy form, including sample ID, external pathologies (only lumps, growths, ulcers, fin erosion), and internal pathologies noted.
- Tabulated results in computer-readable form (*e.g.*, diskette) included in the same shipment as the hard-copy data, but packaged in a diskette mailer to prevent damage. Data must be provided in a format acceptable to the Province Information Manager for transfer to the Province database.
- All QA/QC data (*e.g.*, results of internal and external QC checks) must be submitted by the laboratory as part of the data package, but should be included in separate tables and files from the actual data.

9.4.3 Data Evaluation Procedures

It is the responsibility of the Province Manager to acknowledge initial receipt of the data package(s), verify that the four data evaluation steps identified in the following paragraph are completed, notify the analytical laboratory (or contract field coordinator) of any additional information or corrective actions deemed necessary as a result of the Province's data evaluation, and, following satisfactory resolution of all "corrective action" issues, take final action by notifying the laboratory or field operations coordinator in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for additional personnel (*e.g.*, the Province QA Coordinator) to assist the Province Manager in the technical evaluation of the submitted data packages. While the Province Manager has ultimate responsibility for maintaining official

contact with the analytical laboratory and verifying that the data evaluation process is completed, it is the responsibility of the Province QA Coordinator to closely monitor and formally document each step in the process as it is completed. This documentation should be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist should be supplemented with detailed memos to the project file (both hardcopy and in electronic format) outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package should commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten. The following steps are to be followed and documented in evaluating EMAP-E data:

1. Checking data completeness (verification)
2. Assessing data quality (validation)
3. Assigning data qualifier codes
4. Taking final actions

Checking Data Completeness

The first part of data evaluation is to verify that all required information has been provided in the data package. For field-generated data (*i.e.*, fish identification, enumeration, and length measurements), the crew chief must review all data files to assure they are complete and correct prior to uploading the data to the Field Operations Center. Once the data are received at the FOC, the Virginian Province data librarian should perform a 100% comparison of the electronic files to the original hard-copy datasheets, followed by an additional 10% check. These steps serve not only to ensure that all data contained on the datasheets are present in the database, but also as a check against transcription errors.

EMAP-E laboratories are expected to submit data which have already been tabulated and 100% checked for accuracy. The submitted data will be compared to the data expected based on field observations (*i.e.*, there should be gross external pathology data for each fish sent in for examination). The Province Manager should contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information

was omitted because required analyses were not completed, the laboratory should provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Assessing Data Quality

Data validation, or the process of assessing data quality, can begin after Province personnel have verified that the data package is complete and free of transcription errors. For fish community data, the first step in validation will be automatic range checks. For example, all occurrences of each species are compared to the maximum and minimum latitudes and salinity tolerances, and maximum length for that species. These ranges will be determined from well established sources. If a species is reported from a location where it would not be expected (based on salinity and latitude), or the reported length exceeds the maximum length expected for that species, the record will be flagged for further investigation. This can include checking the record against the original datasheet, checking the taxonomy QA results if applicable, or questioning the crew chief. If no explanation can be identified, the original record will remain unchanged. An additional verification step that must be performed is a check on the trawl duration and speed. A trawl duration between 8 and 12 minutes and a speed between 1 and 3 knots is considered acceptable. Data collected from any trawl that did not meet these acceptability criteria will be rejected.

During the fish data validation process, the results of the laboratory confirmation of the fish species and pathology identifications will be reviewed. These results will be used to improve training in subsequent years, by increasing emphasis on those species and/or pathologies which were consistently misidentified by the field personnel. The fish species which were misidentified will be corrected in the database with the approval of the Province QA Coordinator. Data qualifier codes also will be assigned to the fish pathology results, as described in the following section.

Assigning Data Qualifier Codes

The independent laboratory confirmation of each pathology noted by the field crews will be used to qualify these results in the database. The database codes are self-explanatory (Table 9-1) and are assigned based on whether or not a given pathology was reviewed and confirmed by the laboratory experts.

Table 9-1. Qualifier codes assigned to fish pathology data.

Code	Definition
FP-A	LUMP not observed in field and not observed by laboratory pathologist
FP-B	LUMP not observed in field but was observed by laboratory pathologist
FP-C	LUMP observed in field but not confirmed by laboratory pathologist
FP-D	LUMP observed in field and confirmed by laboratory pathologist
FP-E	LUMP observed in field, but fish not examined by laboratory pathologist
FP-F	LUMP not observed in field, fish not examined by laboratory pathologist
FP-G	GROWTH not observed in field and not observed by laboratory pathologist
FP-H	GROWTH not observed in field but was observed by laboratory pathologist
FP-I	GROWTH observed in field but not confirmed by laboratory pathologist
FP-J	GROWTH observed in field and confirmed by laboratory pathologist
FP-K	GROWTH observed in field, but fish not examined by laboratory pathologist
FP-L	GROWTH not observed in field, fish not examined by laboratory pathologist
FP-M	ULCER not observed in field and not observed by laboratory pathologist
FP-N	ULCER not observed in field but was observed by laboratory pathologist
FP-O	ULCER observed in field but not confirmed by laboratory pathologist
FP-P	ULCER observed in field and confirmed by laboratory pathologist
FP-Q	ULCER observed in field, but fish not examined by laboratory pathologist
FP-R	ULCER not observed in field, fish not examined by laboratory pathologist
FP-S	FIN EROSION not observed in field and not observed by laboratory pathologist
FP-T	FIN EROSION not observed in field but was observed by laboratory pathologist
FP-U	FIN EROSION observed in field but not confirmed by laboratory pathologist
FP-V	FIN EROSION observed in field and confirmed by laboratory pathologist
FP-W	FIN EROSION observed in field, but fish not examined by laboratory pathologist
FP-X	FIN EROSION not observed in field, fish not examined by laboratory pathologist
FP-Y	Fish not examined for gross external pathology

Taking Final Action

Upon completion of the above steps, a report summarizing the QA review of the data package should be prepared, samples should be properly stored or disposed of, and laboratory data should be archived both in a storage file and in the database. Technical interpretation of the data begins after the QA review has been completed.

Reports documenting the results of the QA review of a data package should summarize all conclusions concerning data acceptability and should note significant quality assurance problems that were found. These reports are useful in providing data users with a written record on data concerns and a documented rationale for why certain data were accepted as estimates or were rejected. The following specific items should be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.

- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA Plan.

Fish species identification, enumeration, length measurement and pathology QA results will be included in the annual Program Quality Assurance Report and will also become a permanent part of the database documentation (*i.e.*, the metadata). The QA/QC data collected by the Program will be used not only to assess the quality of individual measurements, but ultimately to assess the comparability of data generated by multiple laboratories and field crews.

SECTION 10

WATER QUALITY MEASUREMENTS

10.1 OVERVIEW

This section presents EMAP-Virginian Province QA/QC protocols and requirements for water quality measurements, from collection to final validation. Collection and analysis methods are documented in the 1993 Field Operations and Safety Manual (Reifsteck *et al*. 1993). With the exception of Total Suspended Solids, all data are generated by the field crews.

Characterization of the water column is accomplished using the Seabird SBE 25 Sealogger® CTD to obtain point-in-time, vertical profiles of temperature, salinity, dissolved oxygen, pH, light transmission, chlorophyll a fluorescence, and photosynthetically active radiation (PAR). A hand-held dissolved oxygen meter manufactured by Yellow Springs Instruments (YSI®) is used to make an additional point measurement of surface and near-bottom dissolved oxygen as a check on, and back-up to, the Seabird CTD measurement. A single surface water sample is obtained at each station for the determination of Total Suspended Solids (TSS) concentration.

Quality control of the water column measurements made with these electronic instruments has several aspects: calibration, QC checks on the calibration, QC checks prior to deployment, and systematic review of the resultant data and QC results. Calibration checks are conducted after the initial calibration and at regular intervals to determine the need for recalibration.

10.2 QUALITY CONTROL PROCEDURES: FIELD MEASUREMENTS

The SeaBird CTD is a sophisticated instrument designed to collect high-quality data for the parameters measured. Intense training of all personnel expected to operate this instrument is necessary to assure reliable operation and acceptable data. Crew chiefs and any other potential operators must be certified in the use of this instrument during training.

The 1990 EMAP-NC Demonstration Project in the Virginian Province shed light on several CTD deployment problems that had an adverse effect on the performance of the dissolved oxygen sensor. The most commonly encountered problems were: 1.) air bubbles trapped in the dissolved oxygen plumbing loop, 2.) mud being drawn through the conductivity cell and into the plumbing loop upon contact of the instrument with the bottom, and 3.) insufficient thermal equilibration time of the dissolved oxygen sensor. Deployment procedures were modified to eliminate these problems. Protocols specified in the 1993 Field Operations and Safety Manual (Reifsteck *et al.* 1993) must be followed to assure data quality and equipment maintenance.

A YSI Model 58 dissolved oxygen meter will be used to measure the dissolved oxygen concentration at the surface and in water collected in a *Go-Flo*® bottle from approximately one meter off the bottom at each station at the same time the Seabird CTD is deployed. Where possible, the *Go-Flo*® should be attached to the CTD to assure comparability. Comparison of the YSI and CTD dissolved oxygen measurements provides a check on the operation of the CTD dissolved oxygen sensor during deployment. In addition, the YSI meter is used for side-by-side QC checks of the Seabird CTDs (once each week).

All water quality measurement activities will be monitored during field crew certification and during QA audits or inspections conducted by senior Program personnel.

10.2.1 Instrument Calibration

Dissolved oxygen and pH sensors on the CTD must be calibrated under controlled laboratory conditions by trained technicians following procedures specified by the manufacturer. For the dissolved oxygen sensor, a two point calibration procedure utilizing a zero adjustment (sodium sulfite solution or nitrogen gas) and a slope adjustment with air-saturated freshwater is employed. The pH probe is calibrated at three points using pH 4, 7 and 10 standard buffer solutions.

Calibrations will be conducted prior to the field sampling and as needed throughout the field season. Immediately following calibration, the dissolved oxygen and pH sensors should be checked for accuracy using Winkler titrations and pH standards, respectively. The instruments' fluorometers are calibrated against algal cultures of known chlorophyll a concentration to assure comparability among units and between years. Temperature, conductivity, light

transmission, and PAR sensors are calibrated by their manufacturers. If calibration checks of these sensors reveal a problem (see the following section), the instrument should be returned to the manufacturer for troubleshooting and/or recalibration.

The YSI dissolved oxygen meters must be calibrated immediately prior to use at each station using the water-saturated air calibration procedure recommended by the manufacturer.

10.2.2 Instrument Calibration Checks

Performance checks should be conducted on the CTD units at the beginning and end of the field season. This procedure involves setting up the four CTD units to simultaneously log data in a well-mixed seawater tank. Overall variability among instruments should be assessed by comparing the simultaneous readings in the tank. The accuracy of the dissolved oxygen measurements can be assessed by comparing the CTD readings against Winkler titration values. The accuracy of the CTD salinity (conductivity) measurements is assessed through comparison with readings obtained with a laboratory salinometer (Guildline AutoSal Model 8400) calibrated with IAPSO Standard Seawater (a.k.a. "Copenhagen" water). The accuracy of the CTD temperature measurements is assessed by comparisons against a NIST-certified thermometer. The instruments should then be removed from the tank and further tested: the transmissometer and fluorometer voltage endpoints (open and blocked light path) are recorded as described by the manufacturer, and the pH sensor readings are checked using three standard pH buffer solutions (pH 4, 7 and 10).

Field QC checks of the CTD temperature, salinity, dissolved oxygen and pH readings must be conducted at least once each week. For this weekly check, real-time CTD readings from just below the surface should be compared to simultaneous measurements with a thermometer, refractometer, and calibrated YSI dissolved oxygen meter. The pH readings are checked using the pH 10 standard buffer solution. If maximum acceptable differences are exceeded (Table 10-1), the CTD instrument must be checked thoroughly and a determination made of the need for recalibration. If it is determined that a probe is malfunctioning and/or requires recalibration, the instrument must be sent back to the Virginian Province Field Operations Center and replaced with a back-up unit.

Calibration QC checks of the YSI meter should be conducted at weekly intervals in the mobile laboratories. Following calibration, the YSI probe should be immersed into a bucket of air-saturated water (bubbled at least 12 hours) and allowed to stabilize. The dissolved oxygen of the water bath is determined by Winkler titration and compared to the YSI reading. The temperature of the water bath should be measured with an alcohol thermometer and compared to the YSI temperature reading. If the dissolved oxygen or temperature difference exceeds the specified limits (Table 10-1), the instrument must be checked thoroughly and a determination made of the need for recalibration or oxygen sensor replacement.

A Hach digital titrator is employed for performing Winkler titrations. This method employs a concentrated solution of sodium thiosulfate as the titrant, therefore, small errors in the delivery of the titrant can cause a significant effect on the final DO value calculated. All personnel conducting titrations must be throughly trained in the operation of the titrator, and demonstrate proficiency during training. In addition, each time a set of samples is titrated, the titrator and thiosulfate cartridge must be standardized against an Iodide-Iodate solution.

Table 10-1. Maximum Acceptable Differences for Instrument Field Calibration Checks

Instrument	Frequency of Check	Parameter	Checked Against	Maximum Acceptable Difference
Seabird CTD	Once each week	Temperature	Thermometer	± 2 °C
		Salinity	Refractometer	± 3 ppt
		DO	YSI meter	± 0.5 mg/L
		pH	pH buffer solution	± 0.5 units
YSI D.O. Meter	Once each week	D.O.	Winkler titration	± 0.5 mg/L
		Temperature	Thermometer	± 2 °C

10.2.3 Instrument Deployment Checks

Each CTD cast data file must be reviewed in the field immediately for evidence of deployment problems. A standard check on the data file should consist of a comparison of the downcast versus the upcast for all parameters, with particular attention to dissolved oxygen, salinity and light transmission. The dissolved oxygen profile should be further evaluated by comparing the surface dissolved oxygen values at the beginning and end of the cast, and by comparing the surface and bottom dissolved oxygen values to those recorded by the hand-held YSI meter. If either of these dissolved oxygen differences exceed 0.5 mg/L, the field crew should recalibrate the YSI and redeploy the CTD to obtain a second profile. If the deployment QC criteria are still not met on the second CTD profile, the field crew should still save the data, but the dissolved oxygen values used in the assessment of water quality will be those from the YSI. The field crew should determine the cause of the discrepancy and either make the necessary repairs in the field or ship the instrument back to the field operations center for servicing. Salinity and temperature should also be checked at the surface and bottom using a refractometer and thermometer, respectively.

10.3 QUALITY CONTROL PROCEDURES: TOTAL SUSPENDED SOLIDS

A surface water sample should be obtained at each station to determine the concentration of Total Suspended Solids. This sample should be collected during the surface soak of the CTD according to the protocols outlined in the Field Operations and Safety Manual (Reifsteck *et al*. 1993). This sample should be placed on ice immediately following collection and shipped at the same temperature (4 °C).

Upon receipt of the sample at the laboratory, the sample custodian must log-in the sample and assure proper storage (4 °C). Strict adherence to the protocols outlined in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision) is mandatory. Samples must be stored for no longer than three months prior to analysis.

The analytical balance and drying oven used in the analysis should be calibrated at least monthly. Quality assurance for the TSS analysis procedures should be accomplished primarily by analyzing a randomly selected subset of 10% of the samples in each batch in duplicate, as described in full detail in the EMAP-E Laboratory Methods Manual (U.S. EPA 1992, in revision). If the relative percent difference (RPD) between the duplicate values is greater than 10%, then a third analysis must be completed by a different technician. The values closest to the third value should be entered into the database. In addition, all the other samples in the same batch must be reanalyzed, and the

laboratory protocol and/or technician's practices should be reviewed and corrected to bring the measurement error under control. If the RPD differs by less than 10%, the original value should not be changed and the analysis process can be considered in control. The RPD is calculated as follows:

$$\text{Relative Percent Difference (RPD)} = \frac{C1 - C2}{(C1 + C2)/2} \times 100$$

where: C1 is the larger of the duplicate results for a measurement

C2 is the smaller of the duplicate results for a measurement

10.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

10.4.1 Sample Tracking

EMAP-E information management personnel have developed a comprehensive system for barcode labeling of sample containers, recording sampling information in the field, and tracking sample shipments. A complete description of this system is provided in the EMAP-E Information Management Plan (Adams *et al*. 1993) and is also summarized in Section 11 of this plan. Field crews must carefully and thoroughly complete all shipment datasheets and transmit this information to the Field Operations Center during the electronic transfer of data.

The analytical laboratory responsible for processing the TSS samples must designate a sample custodian who is authorized to check the condition of and sign for incoming field samples, obtain documents of shipment, and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the Province Information Management Center. The use of barcode labels and readers provided by the Province will facilitate this process. There must be clearly-defined custody procedures for sample handling, storage, and disbursement in the laboratory.

10.4.2 Data Reporting Requirements

Data for the electronic water quality measurements exist in the form of computer files which are entered into the field computer automatically at the time of collection. Crew chiefs must review these data prior to the electronic transfer of the files to the Field Operations Center. Hard-copy original datasheets must be returned to the Field Operations Center no later than the end of the crew's work shift.

For the TSS measurements, only laboratory data which have met QA requirements should be submitted to EMAP. When QA requirements have not been met, the sample should be reanalyzed and only the results of the reanalysis submitted, provided they are acceptable. Each data package submitted by the laboratory should consist of the following:

- A cover letter providing a brief description of the procedures and instrumentation used, as well as a narrative explanation of analytical problems (if any), departures from protocols, or failure(s) to meet required quality control limits.

- Tabulated results in hard-copy form, including sample ID, filter weights, total weights (filter + sample), volume of water filtered, and concentration of TSS in milligrams per liter.

- Tabulated results in computer-readable form (*e.g.*, diskette) included in the same shipment as the hard-copy data, but packaged in a diskette mailer to prevent damage. Data must be provided in a format acceptable to the Province Information Manager.

- Results for all QA/QC samples (*e.g.*, results of duplicate analyses) must be submitted by the laboratory as part of the data package, but should be included in tables and files separate from the actual data.

No QA qualifier codes or "flags" are currently acceptable for TSS data. QA codes for water column measurements are assigned during data evaluation at the Field Operations Center.

10.4.3 Data Evaluation Procedures

It is the responsibility of the Province Manager to acknowledge initial receipt of the data package(s), verify that the four data evaluation steps identified in the following paragraph are completed, notify the analytical laboratory (or contract field coordinator) of any additional information or corrective actions deemed necessary as a result of the Province's data evaluation, and, following satisfactory resolution of all "corrective action" issues, take final action by notifying the laboratory or field operations contractor in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for additional personnel (*e.g.*, the Province QA Coordinator) to assist the Province Manager in the technical evaluation of the submitted data packages. While the Province Manager has ultimate responsibility for maintaining official contact with the analytical laboratory and verifying that the data evaluation process is completed, it is the responsibility of the Province QA Coordinator to closely monitor and formally document each step in the process as it is completed. This documentation should be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist should be supplemented with detailed memos to the project file outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package should commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten. The following steps are to be followed in evaluating EMAP-E data:

1. Checking data completeness (verification)
2. Assessing data quality (validation)
3. Assigning data qualifier codes
4. Taking final actions

Checking Data Completeness

The first part of data evaluation is to verify that all required information has been provided in the data package. For field-generated data (*i.e.*, water quality measurements), the crew chief must review all data files to assure

they are complete and correct prior to uploading the data to the Field Operations Center. Once the data are received at the Center, the Virginian Province Data Librarian should perform a 100% comparison of the electronic files to the original hard-copy datasheets, followed by an additional 10% check. These steps serve not only to ensure that all data contained on the datasheets are present in the database, but also as a check against transcription errors.

EMAP-E laboratories are expected to submit data which have already been tabulated and 100% checked for accuracy. Data received from the analytical laboratory should be compared to the data expected based on field observations (*i.e.*, there should be a TSS value for each sample shipped). The Province Manager should contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory should provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Because the CTD profile consists of an electronic file, only a small portion of which is recorded on hard-copy data sheets, an additional step is required in the verification of these data. This step consists of a check to verify that the CTD file is associated with the correct station and event. Although the field computer system has been designed to virtually eliminate this error, this check should still be conducted. The bottom depth, DO, and salinity values in the CTD file should be compared to those recorded by the field crew on the hard-copy data sheet to assure the file was correctly identified. This step can be automated. DO and salinity values should match exactly, and the CTD bottom depth should match the fathometer reading within 3 meters. Any CTD file that does not match recorded values should be flagged for investigation.

Assessing Data Quality

Data validation, or the process of assessing data quality, can begin after Province personnel have determined that the data package is complete. Each CTD profile must be examined, both manually and via automatic range checks, as part of the validation. Plots of depth versus dissolved oxygen, salinity and temperature should be examined to determine if there is a visible lag between the depth and these parameters as evidenced by the separation of downcasts and upcasts through the pycnocline. At a well-mixed station, there will not be a visible lag in these parameters and alignment is unnecessary. For those profiles which are misaligned, a delay factor for oxygen and or

salinity/temperature (averaging 1 second for salinity/temperature and 5 seconds for dissolved oxygen) should be applied to the raw data file using the Seabird "ALIGNCTD" software. The file should then be reprocessed and plotted and the entire process repeated with different delays until the upcast and down cast align at the pycnocline. The analyst conducting this operation must be qualified in the use of the SeaBird software and must understand the scientific aspects of water quality measurements.

Each CTD cast also must be visually inspected to identify any unusual patterns or spikes that necessitate further review. This can be performed in conjunction with the alignment discussed above. Specific parameters which should be checked are:

- Amount of time at the surface - should be at least 120 seconds;
- Stability of dissolved oxygen at the end of the surface soak - readings for the last 30 seconds prior to the downcast should not vary by more than 0.5 mg/L;
- Stability of the dissolved oxygen values at the beginning and end of the bottom soak - difference should not exceed 0.5 mg/L;
- Stability of the salinity values at the beginning and end of the bottom soak - values should not differ by more than 1 ppt;
- Unexpected patterns or trends in the downcast or upcast (*e.g.*, spikes or dissolved oxygen values increasing with depth);
- A match between downcast and upcast values (compare the last dissolved oxygen record in the pre-deployment surface soak with the last record in the post-deployment surface soak. Flag if the difference is greater than 0.5 mg/L);
- Amount of time at the bottom - should be at least 120 seconds;
- Indications that CTD was lowered into the sediments (large change in oxygen and/or salinity, or a spike in light transmission values).

In addition to examining the profiles themselves, the following range checks should be conducted (either manually or automatically) on the downcast and bottom soak values:

- Depth - acceptable range = 0.3 - 50 meters,
- Temperature - acceptable range = 10 - 35°C,
- Salinity - acceptable range = 0 - 35 ppt,
- Dissolved Oxygen - acceptable range = 0 - 15 mg/L,

- pH - acceptable range = 6 - 11 pH units,
- Light Transmission - acceptable range = 0 - 100%,
- Fluorescence - acceptable range = 0 - 30 units,
- PAR - acceptable range = 0 - 6000 microeinsteins s^{-1} m^{-2},
- Sigma-t - acceptable range = 0 - 25.

Any values falling outside of these ranges should be flagged for investigation. The values and flags should be output in a QA/QC report for each cast.

Assigning Data Qualifier Codes

After the above checks are made, a database QA code should be assigned to the cast. A listing of these codes is presented in Table 10-2. There are 54 codes describing the acceptability of the different water quality parameters in different sections of the cast. No codes are currently accepted for TSS measurements.

Taking Final Actions

Upon completion of the above steps, a report summarizing the QA review of the data package should be prepared, samples should be properly stored or disposed of, and laboratory data should be archived both in a storage file and in the database. Technical interpretation of the data begins after the QA review has been completed.

Reports documenting the results of the QA review of a data package should summarize all conclusions concerning data acceptability and should note significant quality assurance problems that were found. These reports are useful in providing data users with a written record on data concerns and a documented rationale for why certain data were accepted as estimates or were rejected. The following specific items should be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.

- Summary of all QA data (e.g., field QC checks, calibrations, calibration checks).

- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA Plan.

The water quality QA reports will be included in the annual Program Quality Assurance Report and also will become a permanent part of the database documentation (*i.e.*, the metadata). The QA/QC data collected by the Program will be used not only to assess the accuracy and precision of individual measurements, but ultimately to assess the comparability of data generated by multiple laboratories and field crews.

Table 10-2. QA codes assigned to CTD files.

Code	Definition
C-A	Reject entire CTD cast (all parameters)
C-B	Accept entire CTD cast (all parameters)
C-IA	Reject surface values (all parameters)
C-IB	Reject pre-deploy. soak, accept post-deployment soak (all parameters)
C-IC	Reject entire bottom soak, no bottom values available (all parameters)
C-ID	Reject entire downcast file (all parameters)
C-IE	Reject bottom soak, use last value of downcast (all parameters)
C-IF	Reject average of bottom soak but accept last value (all parameters)
C-IG	Shallow station with pre-deployment soak and bottom soak only (no profile)
C-IH	Shallow station: surface and bottom values equal. Bottom file used for both.
C-II	Depth values questionable
C-IJ	Reject surface dissolved oxygen (pre and post)
C-IK	Reject pre cast dissolved oxygen but accept post cast dissolved oxygen
C-IL	Reject downcast dissolved oxygen
C-IM	Reject bottom dissolved oxygen
C-IN	Reject bottom soak dissolved oxygen but use last value of downcast
C-IO	Reject average bottom dissolved oxygen but use last value of bottom file
C-IP	Reject surface salinity (pre and post)
C-IQ	Reject pre cast saliniity but accept post cast salinity

(continued)

Table 10-2 (continued).

Code	Definition
C-IR	Reject downcast salinity
C-IS	Reject bottom salinity
C-IT	Reject bottom soak salinity but use last value of downcast
C-IU	Reject average bottom salinity but use last record of bottom file
C-IV	Reject surface temperature (pre and post cast)
C-IW	Reject pre cast temperature but accept post cast temperature
C-IX	Reject downcast temperature
C-IY	Reject bottom temperature
C-IZ	Reject bottom soak temperature but use last value of downcast
C-JA	Reject average bottom temperature but use last value of bottom file
C-JB	Reject surface pH (pre and post)
C-JC	Reject pre cast pH but accept post cast pH
C-JD	Reject downcast pH
C-JE	Reject bottom pH
C-JF	Reject bottom soak pH but use last value of downcast file
C-JG	Reject average bottom pH but use last value of bottom file
C-JH	Reject surface PAR (pre and post soak)
C-JI	Reject pre-cast PAR but accept post-cast PAR

(continued)

Table 10-2 (continued).

Code	Definition
C-JJ	Reject downcast PAR
C-JK	Reject bottom PAR
C-JL	Reject bottom soak PAR but use last value of downcast
C-JM	Reject average bottom PAR but use last value of bottom file
C-JN	Reject surface transmissometry (pre and post)
C-JO	Reject pre cast transmissometry but accept post cast transmissometry
C-JP	Reject downcast transmissometry
C-JQ	Reject bottom transmissometry
C-JR	Reject bottom soak transmissometry but use last value of downcast
C-JS	Reject average bottom transmissometry but use last value of bottom file
C-JT	Reject surface fluorescence (pre and post)
C-JU	Reject pre cast fluorescence but accept but accept post cast fluorescence
C-JV	Reject downcast fluorescence
C-JW	Reject bottom fluorescence
C-JX	Reject bottom soak fluorescence but use last value of downcast
C-JY	Reject average bottom fluorescence but use last value of bottom file
C-JZ	Fluorescence off-scale

SECTION 11

INFORMATION MANAGEMENT

11.1 SYSTEM DESCRIPTION

The Information Management System developed for the EMAP-E Program is designed to perform the following functions:

- Document sampling activities and standard methods,
- Support program logistics, sample tracking and shipments,
- Process and organize both field and laboratory data
- Perform range checks on selected numerical data,
- Facilitate the dissemination of information, and
- Provide interaction with the EMAP Central Information System.

A complete and detailed description of the EMAP-E Information Management System (IMS) is provided in Adams *et. al*. (1993) and will not be repeated here.

11.2 QUALITY ASSURANCE/QUALITY CONTROL

Two general types of problems which must be resolved in developing QA/QC protocols for information and data management are: (1) correction or removal of erroneous individual values and (2) inconsistencies that damage the integrity of the data base. The following features of the EMAP-E IMS will provide a foundation for the management and quality assurance of all data collected and reported during the life of the project.

11.2.1 Standardization

A systematic numbering system will be developed for unique identification of individual samples, sampling events, stations, shipments, equipment, and diskettes. The sample numbering system will contain codes which will

allow the computer system to distinguish among several different sample types (*e.g.*, actual samples, quality control samples, sample replicates, etc.). This system will be flexible enough to allow changes during the life of the project, while maintaining a structure which allows easy comprehension of the sample type.

A clearly-written instruction manual on the use of the field computer system will be developed for training field personnel and to allow easy reference in the field. Contingency plans also will be stated explicitly in the event that the field systems fail.

11.2.2 Prelabeling of Equipment and Sample Containers

Whenever possible, sample containers, equipment, and diskettes will be prelabeled to eliminate potential confusion in the field and thereby reduce the number of incorrect or poorly-affixed labels. Containers with all the required prelabeled sample containers, sample sheets, and data diskettes will be prepared for the field crews prior to each sampling event (an event is defined as a single visit by a crew to a sampling site). These containers will be called "event boxes". Each event box will have the event number affixed to it using both handwritten and bar code labels.

11.2.3 Data Entry, Transcription, and Transfer

In addition to paper data sheets, all data collected by field crews are recorded in a series of electronic forms on a laptop computer. There is a one-to-one correspondence between the electronic forms (or records) and the paper forms. Data entered in each field of the electronic forms can be checked automatically by the software, which will then provide a warning when data do not fall in an expected range. In many instances, the use of bar code labels and readers in the field will eliminate the need for manual entry of routine sample information and help avoid transcription errors.

Following the initial entry of data into the field computer system, it is printed onto hard copy and checked 100% against the original paper data sheets. This check is performed by the field crew chief, who may correct transcription errors and ultimately is responsible for assigning an acceptance code to the entered data. Once the data have been checked and accepted by the crew chief, the field personnel no longer have the ability to make changes.

A record of each day's computer activities is kept by the field computer software and used by the communications program to compress the data files before transmission. A 9600 baud, error checking modem, which checks each byte as it's sent and eliminates garbled transmissions, transmits the compressed data files to the VAX computer at the field operations center. Paper data sheets are mailed (or hand carried) to the FOC after all sampling activities for a week have been completed.

On the field operations center VAX computer, a program which is run automatically at a specified time of night (after the field crews have transmitted data) performs the following tasks: 1.) unpack the compressed data files, 2.) distribute the data files to appropriate directories on the VAX, 3.) process and plot CTD profile files, and 4.) parse the incoming data into SAS importable files. A SAS program is subsequently run to process the information and automatically generate reports indicating stations visited and activities performed the previous day. This enables a verification check to be performed in which the information received electronically is compared with what the crews reported doing via a daily phone call. Phone logs are also computerized at the Field Operations Center. If there are discrepancies between the two reports the field crews are notified. The SAS program additionally performs range checks on certain types of critical data. Furthermore, each day's data can be viewed by the Province Manager, Field Coordinator, and/or members of the QA staff.

After all data sheets have been received from a field team for a given window (about 6 days), the Virginian Province data librarian performs a 100% manual check of the data sheets against the electronic data stored on the VAX. Any erroneous data values identified in this check or in the previously-generated SAS reports are changed to correct values, with authorization from the Province QA Coordinator. In addition, suspicious data is flagged for further investigation. Whenever a change to the data is required, the data librarian is required to enter a computerized data change form indicating the data sheet, variable, and reason for change. This information is written to a SAS-importable file and is used in compiling error rate statistics for data entry. When satisfied that the data is 100% correct, the data librarian assigns an acceptance code.

11.2.4 Automated Data Verification

Whenever possible, erroneous numeric data will be identified using automatic range checks and filtering algorithms. When data fall outside of an acceptable range, they will be flagged in a report for review by the Province

Manager, the Province Quality Assurance coordinator (QAC), or their designee. This type of report will be generated routinely and should detail the files processed and the status of the QA checks. The report will be generated both on disk and in hard copy for permanent filing. The Province Manager or Quality Assurance Coordinator will review the report and release data which have passed the QA check for addition to the data base. All identified errors must be corrected before flagged files can be added to a data base. If it is found that the data check ranges are not reasonable, the values should be changed by a written request which includes a justification for the change.

Data base entries which are in the form of codes should be compared to lists of valid values (*e.g.*, look-up tables) established by experts for specific data types. These lists of valid codes will be stored in a central data base for easy access by users. When a code cannot be verified in the appropriate look-up table, the observation should be flagged in a written report for appropriate corrective action (*e.g.*, update of the look-up table or removal of the erroneous code).

11.2.5 Sample Tracking

Real-time tracking of all sample shipments will be performed at the Virginian Province Field Operations Center (FOC). The tracking of sample shipments from the field crews to the analytical laboratories is extremely important in order to minimize loss of samples by the field crews, shipping carrier, or receiving laboratory or as a result of improper packaging. Shipment tracking is performed in two ways: by the transfer of shipment and receipt information via daily telephone calls from the field crews and receiving labs, and by the comparison of electronic shipment and receipt files transmitted to the FOC.

All shipments sent to the analytical laboratories by the field crews will be tracked by Virginian Province FOC personnel using a six- or seven-digit shipment number. These shipment numbers are printed on barcodes for ease of entry into computerized shipment and receipt data sheets. All field samples collected are to be associated with a shipment number, whether they are shipped using a carrier (i.e., UPS or Federal Express) or hand carried to a laboratory by a crew member. The association of field samples with the shipment numbers will make it possible to track numerous individual samples through a single number.

As previously indicated, field crews will be required to inform FOC personnel via telephone of daily field and shipping activities. All shipment numbers, shipment dates, sample types, destinations, and carrier identification numbers listed during the telephone call will be carefully recorded by FOC personnel on a phone log. The information on the phone log will then be entered into a SAS dataset on the VAX computer and will be output by SAS in a daily field activities report.

The analytical laboratories will be instructed to place a telephone call to the FOC upon receipt of an EMAP-E sample shipment. The information transmitted in this telephone call will include the EMAP shipment number, date of receipt, and the condition of the samples. This information will also be entered into a SAS dataset on the VAX and will be included in the daily field activities report. The telephone call from the laboratories will constitute verbal confirmation of shipment receipt. If an analytical laboratory informs the FOC that a sample was missing from the shipment or rejected due to improper processing or packaging, this information will be immediately conveyed to the field coordinator in the FOC.

If verbal confirmation of receipt of a package is not received within three days of the shipment date, the data librarian will place a telephone call to the analytical laboratory to confirm that the shipment was not received. If the shipment has not been received, the field coordinator would contact the carrier to begin a trace of the shipment.

All of the field crews will be required to complete an electronic shipment data sheet in the field computer system. This data sheet will contain general shipment information as well as descriptions of each sample in the shipment. A paper shipment form will be completed if the field computer system is not available; however, the information on this form will be entered into the field computer shipment form when a field computer system becomes available. The computer system will maintain a list of all samples collected by each crew along with the status of each sample (i.e., collected, collected/shipped). When a crew member ships a set of samples and enters the SAMPLEIDs into the shipment program, the field computer system will automatically update the status of each of the samples in the list of samples collected. Upon exiting the shipping program, the crew member will be warned if any samples collected have not yet been shipped, if a SAMPLEID already shipped has been entered a second time, or if there is no record of collection of a SAMPLEID entered in the shipment file. This electronic system will improve the accuracy of the shipment files and facilitate sample tracking by the field crews.

A printout of the computer data sheet or a copy of the hand-written shipment form will be included in all shipments to serve as a packing list. The electronic shipment information will be transmitted to the VAX computer overnight and loaded into SAS datasets. SAS will immediately produce a series of reports from which Field Operations Center personnel can track the status of each sample collected through the shipment process. In addition, a printout of the shipment information will be sent to the Field Operations Center weekly accompanied by diskettes storing copies of the electronic shipment files. Final data archiving will be on optical storage media within 6 months of receipt.

All of the analytical laboratories also are required to transmit an electronic file containing shipment receipt information to the FOC on the day each shipment is received. If a receipt file listing all of the SAMPLEIDs in the shipment is not transmitted to the FOC within several days of the verbal confirmation of receipt, the analytical laboratory will be contacted and requested to submit a file as soon as possible.

The goal of electronic shipment tracking is to automate the tracking of shipments and samples as much as possible. The SAMPLEIDs of all field samples collected are stored in a SAS dataset (SAMPLOG). By comparing electronic shipment and receipt files to each other and to SAMPLOG and the electronic phone log file, it is possible to flag missing or extra samples. Every night during the sampling season after field data have been transmitted by the crews, a series of SAS reports will be automatically output listing the status of all shipments.

Each week during the sampling season, a report of all samples in the sample log not yet listed in a receipt file and all samples listed in receipt files but not in the sample log will be produced to allow the further tracing of "missing" or "extra" samples. The data librarian will account for each sample in this report by examining the raw shipped and receipt files, by reviewing the field data sheets, and by contacting the analytical laboratories. If any corrections to the shipment or receipt datasets must be made (i.e., to correct typographical errors), they will be approved by the Virginian Province QA Coordinator, performed by the data librarian, and documented in a memo.

11.2.6 Reporting

Following analysis of the samples, the summary data packages transmitted from the laboratories will include results, QA/QC information, and accompanying text. If the laboratory has assigned internal identification numbers

to the samples, the results should include the original sample number and the internal number used by the laboratory. Specific data reporting requirements associated with each indicator are discussed in the corresponding section of this plan. Analytical laboratories are responsible for permanent archiving of all raw data used in generating results for a minimum period of seven years.

11.2.7 Redundancy (Backups)

All files in the EMAP-E IMS will be backed up regularly. At least one copy of the entire system will be maintained off-site to enable the information management team to reconstruct the data base in the event that one system is destroyed or incapacitated. In the field, all information will be recorded both on paper data sheets as well as in the computer. All information saved to the hard drive will also be copied to a diskette simultaneously. In addition, at the end of each day the field computers will be "equalized" to assure that the information contained on both are identical. At this point all data will be contained on the hard drives of both field computers and on a diskette. At the EMAP-E Virginian Province Information Management Center in Narragansett, incremental backups to removable disk will be performed on all files which have changed on a daily basis. In addition, backups of all EMAP directories and intermediate files will be performed on a weekly basis to provide a backup in the event of a complete loss of the EMAP-E Information Center facility.

All original data files will be saved on-line for at least two years, after which the files will be permanently archived. Archiving of data will be on a non-volatile medium such as an optical "WORM" disk, and one copy of this will be kept off-site. All original files, especially those containing the raw field data, will be protected so that they can be read only (*i.e.*, write and delete privileges will be removed from these files).

11.3 DOCUMENTATION AND RELEASE OF DATA

Comprehensive documentation of information relevant to users of the EMAP-E IMS will be maintained and updated as necessary. Most of this documentation will be accessible on-line, in data bases which describe and interact with the system. The documentation will include a data base dictionary, access control, and data base directories (including directory structures), code tables, and continuously-updated information on field sampling events, sample tracking, and data availability.

A limited number of personnel will be authorized to make changes to the EMAP-E data base. All changes will be carefully documented and controlled by the senior data librarian. Data bases which are accessible to outside authorized users will be available in "read only" form. Access to data by unauthorized users will be limited through the use of standard DEC VAX security procedures. Information on access rights to all EMAP-E directories, files, and data bases will be provided to all potential users.

The release of data from the EMAP-E IMS will occur on a graduated schedule. Different classes of users will be given access to the data only after it has passed a specified level of quality assurance review. Each group will use the data on a restricted basis, under explicit agreements with the Estuaries Resource Group. The following four groups are defined for access to data:

I. The Virginian Province central group, including the information management team, the field coordinator, the Province Manager, the QA Coordinator and the field crew chiefs.

II. EMAP-Estuaries primary users - ERL-Narragansett personnel, ERL-Gulf Breeze personnel, NOAA EMAP-E personnel, and EMAP quality assurance personnel.

III. EMAP data users - All other task groups within EPA, NOAA, and other federal, state and municipal agencies.

IV. General Public - University personnel and the research community.

Prior to release at level IV (general public), all files will be checked and/or modified to assure that values contain the appropriate number of significant figures. The purpose is to assure that the data released do not imply greater accuracy than was realized. This will be especially important in files where data were summarized. In such cases additional figures beyond the decimal point may have been added by the statistical program during averaging or other manipulations. It will be the responsibility of the Quality Assurance Coordinator to determine the appropriate number of significant figures for each measurement.

Requests for premature release of Virginian Province data will be submitted to the Information Management Team through the Province Manager. The Province Information Manager and the Quality Assurance Coordinator, in consultation with the Province Manager, will determine if the data can be released. The final authority on the release of all data is the Technical Director of EMAP-Estuaries. The long-term goal for the EMAP-E Information Management Team will be to develop a user interface through which all data will be accessed directly on the computer. This will improve control of security and monitoring of access to the data, and it will help ensure that only the proper data files are being accessed.

SECTION 12

QUALITY ASSURANCE REPORTS TO MANAGEMENT

A quality assurance report will be prepared by the Province QA Coordinator following each year's sampling efforts. This report will summarize the measurement error estimates for the various data types using the QA/QC sample data. Precision, accuracy, comparability, completeness, and representativeness of the data will be addressed in this document.

Within 30 days of each audit (field or laboratory), the QA Coordinator will submit a report to the Province Manager. This report will describe the results of the audit in full detail and note any deficiencies requiring management action. The QA Coordinator will monitor the implementation of corrective actions in response to negative findings, and will make regular reports to the Province Manager in this regard.

In addition to the formal reports described above, the Province QA Coordinator will report regularly to the Province Manager on an informal basis, through E-mail, conference calls, and/or direct contact. One of the primary responsibilities of the QA Coordinator is to keep the Province Manager informed of any issue or problem which might have a negative effect on the data collected.

The EMAP-E Program Quality Assurance Coordinator, with assistance from the Province QA Coordinators, will prepare a Quality Assurance Annual Report and Work Plan (QAARWP) for the Estuaries Resource Group. The QAARWP summarizes the quality assurance activities conducted during the previous fiscal year, and describes activities planned for the upcoming fiscal year. This report will be prepared following the guidelines presented in the approved Quality Assurance Management Plan for EMAP (Kirkland, in preparation). The QAARWP will be completed, approved by the EMAP-E Technical Director, and delivered to the EMAP QA Coordinator by September 30 of each year.

SECTION 13

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