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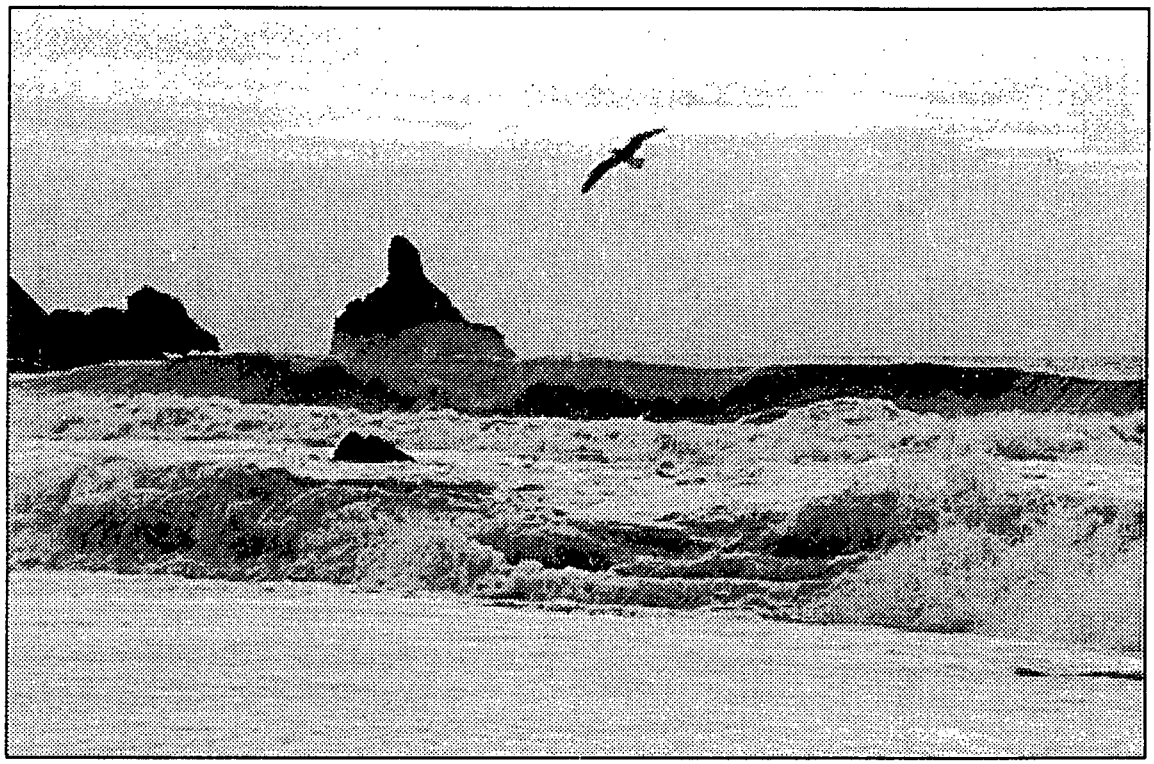

Bay Protection and Toxic Cleanup Program

Quality Assurance Project Plan

STATE WATER RESOURCES CONTROL BOARD

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

COV0034-A

BAY PROTECTION AND TOXIC CLEANUP PROGRAM

QUALITY ASSURANCE PROJECT PLAN

by

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QUALITY ASSURANCE PROJECT PLAN APPROVAL

This Quality Assurance Project Plan (QAPP) was developed to assure that all environmental data generated for the State Water Resources Control Board's (SWRCB) Bay Protection and Toxic Cleanup Program (BPTCP) 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, as well as the philosophy of total quality, to all project participants.

Craig J. Wilson — 7/19/94 Date
BPTCP Contract/Project Manager for SWRCB
Bay Protection and Toxic Cleanup Program
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PREFACE

This Quality Assurance Project Plan (QAPP) was prepared jointly by the California Department of Fish and Game (DFG) and the California State Water Resources Control Board (SWRCB) to insure quality in the scientific components of the Board's Bay Protection and Toxic Cleanup Program (BPTCP). The QAPP was prepared in large part by utilizing many elements, both format and content, of the QAPP for the Environmental Monitoring and Assessment Program (EMAP-Estuaries) for the 1993 Virginian Province, a U.S. Environmental Protection Agency (EPA) program. EMAP's QAPP, and thus the BPTCP's QAPP, follows the general guidelines and specifications provided by the Quality Assurance Management Staff of the U.S. EPA Office of Research and Development and guidelines provided in the EMAP Quality Assurance Management Plan. Because this QAPP will also be used for EMAP monitoring activities in California, a number of tasks or analyses supplemental to the methods necessary for the BPTCP are included in this QAPP. These additional methods are printed in **bold** type, and are contingent upon necessary funding.

The primary objective of this QAPP is to maximize the probability that environmental data collected by the BPTCP will meet or exceed the objectives established for data quality. The QAPP 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 QAPP 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 BPTCP database.

This QAPP has been submitted in partial fulfillment of SWRCB Contract No. 1-165-250-0 from the California State Water Resources Control Board to the California Department of Fish and Game.

The proper citation of this document is:

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ACKNOWLEDGEMENTS

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SECTION 1

INTRODUCTION

1.1 OVERVIEW OF THE BAY PROTECTION AND TOXIC CLEANUP PROGRAM

In 1989 the California Water Code was amended (Sections 13390 through 13396) to create the Bay Protection and Toxic Cleanup Program (BPTCP). The three primary goals of the program are to 1) identify toxic hot spots, 2) develop sediment quality objectives, and 3) remediate hot spots, either through cleanup efforts, mitigation, or prevention. The monitoring which forms a necessary component of each of these goals and the statutory requirements for standard procedures requires the development of a Quality Assurance Project Plan (QAPP). The remainder of this introductory section provides the necessary project description for development of the QAPP's objectives and specific contents. It is organized into subsections covering the working definition of a toxic hot spot, methods for distinguishing natural from human-caused impacts, sampling design, and analysis of results. More details regarding such aspects of the program as indicator and site selection are described in the first status report of the program (SWRCB, 1993).

1.1.1 Hot Spot Definition

A detailed working definition of a known toxic hot spot has been developed that consists of the following five conditions (the full definition is included in Appendix 1):

1. Exceedance of water or sediment quality objectives,
2. Water or sediment toxicity associated with toxic pollutants,
3. Exceedance of tissue contaminant levels established by various agencies for the protection of human health or wildlife,
4. Impairment of resident organisms associated with toxic pollutants, and
5. Degradation of populations or communities associated with toxic pollutants.

(The definition also includes potential hot spots which are determined by concentrations of toxic pollutants above background levels, screening or other test toxicity, elevated tissue levels, or levels in excess of sediment or water quality criteria. Because a conservative approach was adopted in the development of the known toxic hot spot definition, rather stringent criteria have been included. For example, the mere presence of contamination was determined to be insufficient for qualification as a hot spot unless the level is high enough to exceed regulatory standards. Likewise, bioeffects are required to be demonstrated in relation to properly selected reference sites and to occur in association with chemical contamination. Furthermore, several of the criteria require a demonstration of recurrent effects.

Underlying this definition is a weight-of-evidence approach to the combination of the mixture of chemical and bioeffects measures. Since the presence of correlations between many of these measures is unknown at this time, it is conceivable that some sites may qualify as hot spots for some criteria but not for others. Consequently, sites for which a number of criteria are satisfied (e.g., sediment toxicity, benthic degradation, and a positive biomarker test accompanied by high contaminant levels in sediment and tissue) will be considered the highest priority for remediation. It will be necessary, therefore, to monitor some sites for the full mix of chemical and bioeffects measures.

1.1.2 Natural vs. Human-Caused Impacts

Prevention or remediation of hot spots resulting from human activity requires the ability to distinguish between those of natural and human origin. Monitoring designs can produce data that range from the purely correlational (i.e. the simple presence of pollutants in concert with bioeffects) to the carefully performed sediment TIE (or equivalent study for other bioeffects) whereby a specific causal relationship is convincingly established. For the purposes of BPTCP monitoring neither of these extremes was deemed acceptable - simple correlation studies would result in too many false positives (resulting in excessive remediation expenditures) while sediment TIEs or their equivalents would be too time-consuming and would require excessive use of funds from public sources rather than responsible parties.

A compromise between these two extremes settled on the identification and use of reference sites matched for various confounding natural variables. For example, sediment toxicity reference sites were matched for sediment grain size and TOC, the latter being presumed to covary with other possible confounding factors. Similarly, benthic analysis reference sites will be matched for these variables as well as others thought to be relevant (**e.g., dissolved oxygen content, salinity, temperature, pH, and natural toxins, if necessary funding is provided**). In this way, demonstrated bioeffects at a site (relative to a matched reference) will be determined to be associated with toxic chemicals if chemical analysis demonstrates significantly higher levels compared to the reference sites. Because a strict determination of cause-and-effect will not have been achieved (due to its extreme expense), we anticipate that responsible parties will have the opportunity to conduct Toxicity Identification Evaluations as an initial step in site remediation.

1.1.3 Sampling Design

The current design consists of site selection followed by a four-phase sample collection and analysis effort. Site selection is based on previous evidence of contamination, previous evidence of a lack of contamination, or the probability of contamination or its absence based on knowledge of polluting activities in the waterbody; other sites are selected randomly within strata. Staff of the State Water Resources Control Board's Bays and Estuaries Unit are responsible for selection of all sites, for selection of analyses to be performed at each site, for setting a schedule for field collection of samples, for selection of statistical analyses to be performed, and for all other monitoring program plans.

Once sites have been selected, sediment is sampled and tested with a suite of bedded sediment and pore water toxicity tests (referred to as "toxicity screening"). Nontoxic sites are resampled (referred to as a "reference site survey") in an effort to identify a group of potential reference sites that encompass the full range of characteristics (e.g., grain size and TOC) likely to occur among the sites to be retested for toxic hot spot status. "Confirmation" is then performed by means of which the sites with the highest toxicity from screening are

sampled in conjunction with the most appropriate potential reference sites. This third phase of sampling is more intensive than screening, including field replication as well as careful matching with reference sites. Chemical analysis is also emphasized, consisting of a full range of conventional metals and organics analyses on the confirmation sites that emerge as reference and toxic within each stratum (see below for explanation of data analysis methods to distinguish reference from toxic sites). **Attention will also be given to the role of unknown chromatographic peaks as well as naturally occurring toxins, if appropriate funding is provided.** Finally, the fourth phase of sampling consists of benthic collection and, if deemed appropriate, mussel or fish tissue for biomarker analysis (defined as biochemical changes or cell, tissue, or organism pathology). Chemical analysis of sediment will also be performed on sites judged to be impacted and unimpacted using these additional bioeffects measures and similar statistical analysis techniques. The four phases of sample collection are summarized in Table 1-1.

1.1.4 Statistical Analysis

As indicated in Table 1-1, statistical analysis to identify toxic hot spots is a multistage process that relies heavily on ordination analysis (see examples in EcoAnalysis et al., 1992 and Anderson et al., 1988). First, each separate bioeffect measure (toxicity, benthic composition, and biomarker status) is analyzed within relevant strata to determine whether reference and impacted sites can be distinguished. Next, using similar techniques, an effort is made to evaluate whether differences in toxins (conventionally measured, naturally occurring, and unknowns) are associated with the distinction between reference and impacted sites. Finally, the bioeffect-specific analyses are repeated on the combined bioeffects measures to address the weight-of-evidence approach and as an aid in prioritization of remediation efforts. As a result, sites with multiple bioeffects impacts receive more attention.

Table 1-1. Four Phases of Sample Collection for Toxic Hot Spot Identification. Note that not all of these analyses are performed at every site; these are the possible analyses that can be performed.

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1. Toxicity Screening

- Suite of toxicity tests
  - Solid phase (bedded sediment) tests
    - *Rhepoxynius abronius* survival for salinity above 25 ppt
    - *Eohaustorius estuarius* survival for salinity below 25 ppt
    - *Neanthes arenaceodentata* growth for salinity above 20 ppt
  - Liquid phase tests
    - Interstitial water (pore water) tests
      - *Strongylocentrotus purpuratus* fertilization and/or development for salinity above 25 ppt
      - Bivalve (*Mytilus edulis* or *Crassostrea gigas*) larval shell development for salinity below 25 ppt
    - Subsurface water (overlying water) tests
      - *Haliotis rufescens* embryo/larval shell development for salinity above 25 ppt
      - Bivalve (*Mytilus edulis* or *Crassostrea gigas*) larval shell development for salinity below 25 ppt
- Five laboratory replicates with controls (three replicates for a dilution series of pore water)
- Ammonia, hydrogen sulfide, grain size, and TOC measured
- Metals and organics analysis of most and least toxic sites

2. Reference Site Survey

- Sites selected from screening phase that tested nontoxic for a variety of tests
- Nontoxic and toxic sites matched for grain size and TOC
- Repeat sample collection and toxicity testing of these potential reference sites

3. Toxicity Confirmation

- Sites selected from screening phase that tested toxic for any test
- Nontoxic sites from reference site survey (i.e. "reference sites") and toxic sites from screening matched for grain size and TOC

Table 1-1. Continued

- Repeat sample collection and toxicity testing of reference sites and toxic sites
  - Repeat of toxicity screening tests which were positive
  - Three field replicates in addition to five laboratory replicates with controls (three laboratory replicates for pore water dilution series)
  - Ammonia, hydrogen sulfide, grain size, and TOC measured
  - Statistical analysis to distinguish reference from toxic sites within strata
  - Pesticides, PCB, PAH, TBT, metals, and natural toxins measured on sediment from clearly distinguished reference and toxic sites
  - Additional statistical analysis to assess relative chemical contamination of reference and toxic sites (includes unknown peaks)

4. Field Bioeffects Assessment

- Benthic community analysis
  - Site sampling (reference, toxic, random, and other) during the same season each year
  - Five field replicates
  - Field measurement of other factors capable of influencing benthic composition
  - Ordination analysis to distinguish reference from impacted sites within strata (the analysis is conducted on a continually enlarging database as more sites are assessed)
  - Pesticides, PCB, PAH, TBT, metals, and natural toxins measured on sediment from clearly distinguished reference and impacted sites
  - Additional ordination analysis to assess relative chemical contamination of reference and impacted sites within strata (includes unknown peaks)
- Tissue Biomarker Analysis
  - Field and laboratory replicates
  - Field measurement of other factors capable of influencing the biomarker
  - Statistical analysis
  - Chemical analysis
  - Statistical analysis

1.2 QUALITY ASSURANCE PROGRAM FOR BPTCP

The State Water Resources Control Board's Bay Protection and Toxic Cleanup Program will conform with all requirements specified in the EPA mandatory QA guidelines (40 CFR Part 30.500, Stanley and Verner 1983, EPA 1988). As part of this program, every environmental monitoring and measurement project is required to have a written and approved Quality Assurance Project Plan (QAPP).

The QAPP for the State Water Resources Control Board's Bay Protection and Toxic Cleanup Program (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 will 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, EPA 1988) states that the 15 items shown in Table 1-2 should be addressed in the QAPP.

TABLE 1-2. Sections in this report that address the 15 subjects required in a Quality Assurance Project Plan.

Quality Assurance Subject	BPTCP QAPP (this document)
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 3A
Sample custody	Section 3A
Calibration procedures	Section 3B
Analytical procedures	Section 3B and SOP's
Data reduction, validation, and reporting	Section 9
Internal QC checks	Section 5
Performance and system audits	Section 3B
Preventive maintenance	Section 3B
Corrective action	Section 4
QA reports to management	Section 10

SECTION 2
PROJECT ORGANIZATION

2.1 MANAGEMENT STRUCTURE

Overall management of BPTCP monitoring activities will be provided by the Bays and Estuaries Unit of the State Water Resources Control Board (SWRCB). Staff of the SWRCB's Bays and Estuaries Unit are responsible for selection of all sites, for selection of analyses to be performed at each site, for setting a schedule for field collection of samples, for selection of statistical analyses to be performed, and for all other monitoring program design and planning. Expertise in specific analytical techniques and field collection of samples will be provided by the Department of Fish and Game (DFG) and their contracted organizations. DFG's Marine Pollution Studies Laboratories, with headquarters at Moss Landing Marine Laboratories (MLML), has been designated as the principal laboratory for the BPTCP; DFG staff at Moss Landing Marine Laboratories and Granite Canyon Marine Laboratory will provide direction, coordination, and support for all activities. DFG personnel at Moss Landing Marine Laboratories conduct the metals analyses and provide overall database management. DFG's scientific and technical services are primarily supplemented through subcontracts with the following organizations: 1) San Jose State University Foundation -- to conduct sample collection, sample preparation, some metal analyses, benthic analyses, total organic carbon analyses, and grain size analyses (performed at Moss Landing Marine Laboratories), 2) University of California at Santa Cruz -- to conduct toxicity testing (performed at DFG's Granite Canyon Marine Pollution Studies Laboratory) and trace organic chemical analyses (performed at UCSC's Long Marine Laboratory), and 3) EcoAnalysis, Inc. -- to aid in data management and the statistical design and data analysis. Additional services which are subcontracted by DFG include: California State University Long Beach, University of California at San Diego, and University of California at Davis for the development of biomarker tests; and the U.S. Geological Survey for the development of water quality models in the San Francisco Bay region. Figure 2-1 illustrates the management structure for BPTCP monitoring while key personnel are listed in Table 2-1.

FIGURE 2-1. **Management structure for the Bay Protection and Toxic Cleanup Program's scientific component (contracted to the California Department of Fish and Game).**

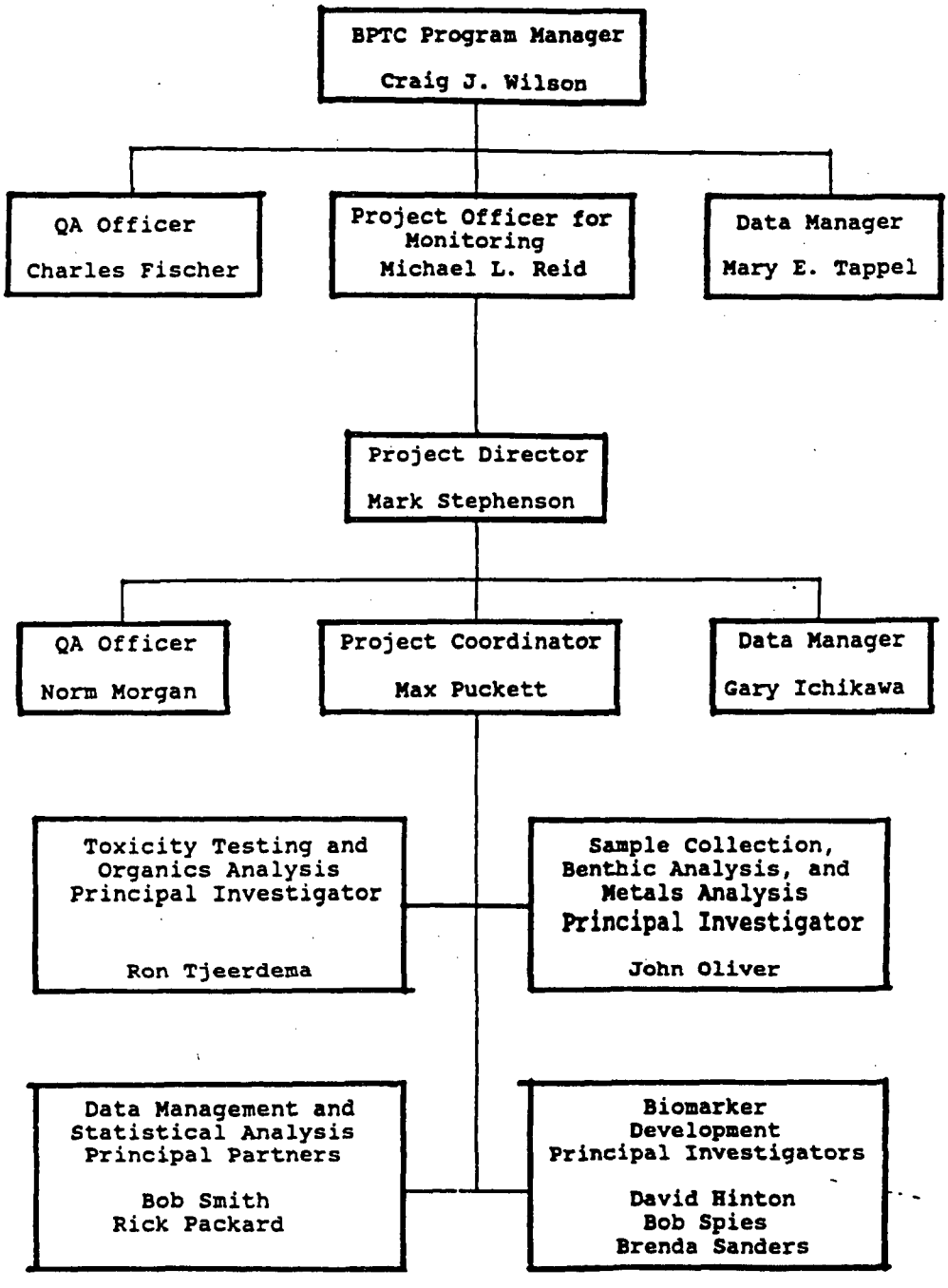

TABLE 2-1. List of key personnel, affiliations, and responsibilities for the BPTCP.

NAME	AFFILIATION (LOCATION)	RESPONSIBILITY
Craig J. Wilson	SWRCB (Sacramento)	SWRCB Program Manager
Mike Reid	SWRCB (Sacramento)	SWRCB Project Off. Monitoring
Charles Fischer	SWRCB (Sacramento)	SWRCB QA Officer
Mary Tappel	SWRCB (Sacramento)	SWRCB Data Manager
Mark Stephenson	DFG-MLML (Moss Landing)	DFG Project Manager
Max Puckett	DFG-GC (Monterey)	DFG Project Coordinator
Norman Morgan	DFG-WPCL (Nimbus)	DFG Project QA Officer
Gary Ichikawa	DFG-MLML (Moss Landing)	DFG Project Data QC Officer
Jon Goetzl	DFG-MLML (Moss Landing)	Furnace Metals Analyses
Kim Paulson	DFG-MLML (Moss Landing)	TBT, Flame Metals; Admin.
James Kanihan	DFG-MLML (Moss Landing)	TBT, Flame Metals
Dave Crane	DFG-WPCL (Nimbus)	Metal Analyses (Se & As)
John Oliver	SJSUF-MLML (Moss Landing)	SJSUF Principal Investigator
Rusty Fairey	SJSUF-MLML (Moss Landing)	SJSUF Sampling Project Manager
Cassandra Roberts	SJSUF-MLML (Moss Landing)	Field Crew/Lab Manager
Eric Johnsen	SJSUF-MLML (Moss Landing)	Field Crew/Fisheries
James Downing	SJSUF-MLML (Moss Landing)	Field Crew/Sampling QC Officer
Ross Clarke	SJSUF-MLML (Moss Landing)	Field Crew/GIS mapping
Jim Oakden	SJSUF-MLML (Moss Landing)	Benthic (& TOC/grain size) Project Manager
Diane Carney	SJSUF-MLML (Moss Landing)	Grain Size & TOC QC Officer
Pat Iampietro	SJSUF-MLML (Moss Landing)	Grain Size and TOC
Carrie Bretz	SJSUF-MLML (Moss Landing)	Benthic Community Analyses & Benthic QC Officer
Mike Gordon	SJSUF-MLML (Moss Landing)	Pore Water Metals Analyses
Ron Tjeerdema	UCSC-LML (Santa Cruz)	UCSC Principal Investigator
John Hunt	UCSC-GC (Monterey)	UCSC Tox Project Officer/QC Off.
Brian Anderson	UCSC-GC (Monterey)	UCSC Tox Project Co-manager
Shirley Tudor	UCSC-GC (Monterey)	Tox Testing Data Manager
Bryn Phillips	UCSC-GC (Monterey)	Tox Testing Analytical Manager
Deborah Holstad	UCSC-LML (Santa Cruz)	Organic Analyses Project Manager
John Newman	UCSC-LML (Santa Cruz)	Organic Analyses & QC Officer
Ed Long	NOAA (Seattle, WA)	BPTCP/NOAA Coop. Agreement
David Hinton	UCD (Davis, CA)	UCD Principal Investigator
Brenda Sanders	CSULB (Long Beach, CA)	CSULB Principal Investigator
Raymond Chen	USGS (Menlo Park, CA)	USGS Principal Investigator
Rick Packard	Ecoanalysis (Ojai, CA)	Ecoanalysis Data Systems Manager
Bob Smith	Ecoanalysis (Ojai, CA)	Ecoanalysis Statistical Systems

Table 2.1 Continued

Abbreviations

SWRCB = California State Water Resources Control Board
DFG = California Department of Fish and Game
MLML = Moss Landing Marine Laboratories
GC = DFG's Granite Canyon Marine Pollution Studies Laboratory
SJSUF = San Jose State University Foundation
UCSC = University of California, Santa Cruz
LML = UCSC's Long Marine Laboratory
NOAA = National Oceanic and Atmospheric Administration
UCD = University of California, Davis
CSULB = California State University Long Beach
USGS = U.S. Geological Survey

SECTION 3

GENERAL FIELD AND LABORATORY OPERATIONS

PART A: SAMPLE COLLECTION AND PROCESSING

3.1 INTRODUCTION

Currently the BPTCP is focused on the identification of Toxic Hot Spots. Later editions of the QAPP will be modified to address both the remediation of hot spots and the development of sediment quality objectives. Part A of this section describes the sampling design for hot spot identification as well as the specific techniques for collection and processing of samples. Because the collection of sediments influences the results of all subsequent laboratory and data analyses, it is important that samples be collected in a consistent and conventionally acceptable manner. **However, because conventional methods may yet be insufficiently tested for the presence of artifacts, the program will include a systematic effort to identify their presence (via comparison with field validation techniques) and subsequently determine their origins**, if authorized and funded by the SWRCB.

3.2 SAMPLING DESIGN

Hot Spot identification consists first of locating sites with the potential for hot spot status (screening) followed by more thorough testing to confirm the site as a hot spot (confirmation). Several strategies are applied to locating sites for followup. First, existing monitoring data is reviewed to identify tissue contaminant sites (principally State Mussel Watch data), sediment contaminant sites (most often associated with waste discharge practices), and, less frequently, bioeffect sites (e.g., toxicity, benthic composition, and biomarkers). An important component of this and other site-location options is the identification of relatively clean sites that can be tested for use as reference sites. A second

option is the examination of previously unsampled sites which are suspected of being either contaminated or clean based on a knowledge of polluting activities. Finally, other sites are sampled in a stratified random manner to allow generalizations regarding the hot spot status of entire waterbodies. For all three options, specific site location information is detailed in contract task orders. With extension of the BPTCP, it is anticipated that a second round of such task orders will eventually be released.

Once sites have been identified for sampling, field collection of sediment is then scheduled. Because toxicity resulting from human activity is not presumed to be heavily influenced by seasonality, collection for this purpose is scheduled throughout the year. In contrast, benthic sampling is scheduled for a relatively small window during the summer due to its seasonal dependence. Because both of these measures will be linked to chemical contamination to qualify for hot spot status, sampling for this purpose will accompany both scheduled events even though this may result in some duplication. Scheduling of biomarker sampling will probably follow that of toxicity testing, but a decision on this will await completion of biomarker development efforts.

Site locations (latitude & longitude) will be pre-determined by agreement with the SWRCB, NOAA, Regional Water Quality Control Boards, and DFG personnel. Changing of the site locations during sediment collection will be allowed only under the following conditions;

1. lack of access to predetermined site,
2. inadequate or unusable sediment (i.e. rock or gravel)
3. unsafe conditions
4. agreement of appropriate staff

All site locations (latitude & longitude), whether altered in the field or pre-determined, will be verified using a Magellan GPS NAV 5000, and the data will be recorded in the field logbook. Once the site location has been established, a temporary buoy may be deployed. If within-site replication is required (confirmation sampling), three samples (stations) will be

taken at each site, one sample per station. A triangle with the buoy as the center point, with approximately 10-meter sides will be visually mapped. The three samples will be taken, one at each point of the triangle, and a separate data sheet including latitude and longitude information will be completed. The boat may be anchored at each point to reduce drifting from position.

3.3 RECORD KEEPING

3.3.1 Field Logbook

A designated person will be responsible for recording data in a waterproof field logbook. The field logbook will include;

- date and time of start of sampling
- name of personnel, name of boat
- location of station (latitude & longitude)
- station description (DFG number, photos)
- type of grab used
- field observations (weather, water conditions)
- station depth
- number of grabs necessary and amount sampled
- type of analyses to be performed
- salinity and temperature
- visual characteristics (texture, benthos, odor, sheens)

Pending funding and authorization, the following additional field data shall also be collected and recorded: dissolved oxygen, stratification profiles of salinity and temperature, pH, secchi depth, redox potential discontinuity depth, and possibly other parameters.

3.3.2 Chain-of-records

A Chain-of-Record form will accompany every sample. Each person releasing a sample will sign and date the form and get the receiver's signature, with date and time, keeping one copy and giving one copy to receiver. Chain-of-records documents will be maintained for each station. Each form will be a record of all samples taken for each station. IDORG (a unique identification number for only that sample), DFG station numbers and station names, leg number (sample collection trip batch number), and date collected will be included on each sheet.

3.3.3 Authorization/Instructions to Process Samples

Standardized forms entitled "Authorization/Instructions to Process Samples" accompany the receipt of any samples by any participating laboratory. These forms are completed by DFG personnel, or its authorized designee, and are signed and accepted by both the DFG authorized staff and the staff accepting the samples on behalf of the particular laboratory. The forms contain all pertinent information necessary for the laboratory to process the samples, such as the exact type and number of tests to run, number of laboratory replicates, dilutions, exact eligible cost, deliverable products (including hard and soft copy specifications and formats), filenames for soft copy files, expected date of submission of deliverable products to DFG, and other information specific to the lab/analyses being performed.

3.3.4 Labels

Labels will be fastened to outside and/or inside sample container. No jars will contain handwritten labels. As an extra check on proper labeling, all jars will be pre-labeled before samples are aliquoted. Labels will contain the following information:

-IDORG number

-DFG station number

-station name

-leg sampled

-date sampled

3.4 COLLECTION OF SAMPLES AND FIELD MEASUREMENTS

3.4.1 Training Program and Field QA Audits

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 geographic areas. Each crew consists of a boat captain, chief scientist, and a minimum of one technician. Minimum qualifications for chief scientists will 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 will be an experienced boat handler, preferably holding a captain's license.

All the sampling equipment (*e.g.*, boats, instruments, grabs, nets, etc.) will be used extensively during "hands-on" training sessions (actual field sample collection trips). By the end of the sampling trip, all crew members must demonstrate proficiency in all the required sampling activities.

In addition to in-field and in-laboratory training, all crews will be evaluated on their field performance during an annual field QA audit conducted by BPTCP DFG personnel. If any deficiencies within a crew are noted during this QA audit, they will be remedied prior to continued field sampling. This can be accomplished by additional training or by changing the crew composition. It is the responsibility of the SJSUF Project Manager/QC Coordinator to develop and implement internal training and QA audit "checklists". Copies must be maintained in a central file by SJSUF of all internal training and QA audit reports completed. When requested, these records must be accessible to or copies provided to the DFG QA officer or designee.

3.4.2 Collection of grab-deployed samples

Devices for subtidal surficial sampling vary greatly. The primary criterion for an acceptable sampling device is that it consistently collect undisturbed samples to a depth of 2-cm below the sediment surface without contaminating the samples. The size of the device will depend upon the amount of sediment needed and the size of the boat used. Other criteria for acceptable samples for collection of undisturbed sediment include:

- create a minimal bow wake when descending
- form a leak proof seal when the sediment sample is taken
- prevent winnowing and excessive sample disturbance when ascending
- allow easy access to the sample surface

For this study the primary method of sediment collection will be a Young-modified Van Veen grab. Modifications include a Kynar coat covering the sample box and jaws. Approximately 20 to 30 sites will be sampled every sampling trip (a "leg"). Trips will be spaced 2-3 weeks apart to allow for toxicity tests to be run. Replicate quality control samples for sediment chemistry will be taken at 5% of the total sites sampled, if authorized and funded by the SWRCB.

3.5 SAMPLE ACCEPTABILITY CRITERIA

After the filled sampler is secured on the transom, or gunnel, or deck, the sediment sample will be carefully inspected. The following acceptability criteria will be met:

- o Sampler is not over-filled (i.e., the sediment surface is not pressed against the top of the sampler).
- o Overlying water is present, indicating minimal leakage.
- o Overlying water is not excessively turbid, indicating minimal sample disturbance.
- o Sediment surface is relatively flat, indicating minimal sample disturbance.
- o Desired penetration depth is achieved (i.e., 20 cm).
- o Sample is muddy (>30% fines), not sandy or gravelly.
- o Sample does not include excessive shell and organic debris.

If a sample does not meet all the above criteria, it will be rejected.

3.6 CLEANING PROCEDURES

This section describes cleaning of sediment sampling equipment, sediment storage containers, and sediment sampler.

3.6.1 Field equipment

All sampling equipment (i.e., containers, container liners, scoops, water collection bottles) will be made of non-contaminating materials and will be pre-cleaned and protectively packaged prior to entering the field. Sample collection gear and samples will only be handled by personnel wearing non-contaminating polyethylene gloves. All sample collection equipment (excluding the sediment sampler) will be cleaned by using the following sequential process:

> Two-day soak and wash in Micro (brand) detergent, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Type II--Milli-Q (brand)-- water rinses, air dry, three petroleum ether rinses, and air dry.

All cleaning after the Micro (brand) detergent step is performed in a positive pressure "clean" room to prevent airborne contaminants from contacting sample collection equipment. Air supplied to the clean room is filtered.

The sediment sampler is cleaned prior to entering the field by utilizing the following sequential steps: a vigorous Micro (brand) detergent wash and scrub, a tap-water rinse, air dry, a 10% HCl or HNO_3 rinse, and a petroleum ether rinse.

3.6.2 Sample storage containers

Sample storage containers are cleaned in accordance with the type of analysis to be performed upon its contents. All containers will be cleaned in a positive pressure "clean" room with filtered air to prevent airborne contaminants from contacting sample storage containers.

Containers for trace metal analysis media (sediment, archive sediment, pore water, and subsurface water) are cleaned by: a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Type II--Milli-Q (brand)-- water rinses, and air dry.

New containers for synthetic organic analysis media (sediment, archive sediment, pore water, and subsurface water) and additional teflon sheeting cap-liners are cleaned by: a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Type II--Milli-Q (brand)-- water rinses, air dry, three petroleum ether rinses, and air dry.

Acid volatile sulfide analysis sediment containers are cleaned by: a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Type II--Milli-Q (brand)-- water rinses, and air dry.

Total organic carbon and grain size analysis sediment containers are cleaned by a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Type II--Milli-Q (brand)-- water rinses, three rinses with petroleum ether, followed by air drying.

3.6.3 In-field cleaning

To avoid cross-contamination, all equipment used in sample handling will be thoroughly cleaned before processing any sample or portion thereof. The sediment sampler will be cleaned prior to sampling a site by: rinsing all surfaces with seawater, scrubbing all sediment sample contact surfaces with Micro (brand) detergent, rinsing all surfaces with seawater, rinsing sediment sample contact surfaces with 10% HCl or HNO_3, and rinsing all sediment sample contact surfaces with methanol. If sites have multiple stations, the sediment sampler will be scrubbed and cleaned between stations in the same manner as it is between sites.

The sediment sampler will be scrubbed with seawater between successive deployments to remove adhering sediments from contact surfaces possibly originating below the sampled layer, thus preventing contamination from areas beyond target sampling area. Sampling procedures will attempt to avoid exhaust from any engine aboard any vessel involved in sample collection. An engine will be turned off when possible during portions of the sampling process where contamination from engine exhaust may occur.

Trace metal-free and synthetic organic-free polystyrene scoops are used to transfer sample mud from the grab to the sample holding container. The sample holding container will be composed of noncontaminating polyethylene or polycarbonate.

3.7 SEDIMENT SAMPLE COLLECTION

3.7.1 Sediment sample collection utilizing grab sampler

Before sub-samples from the grab sampler are taken, the overlying water will be removed. One method of removing this water is by slowly siphoning it off or using a turkey baster to pipette out overlying water. Other methods, such as decanting the water or slightly opening the sampler to allow the water to escape, will be done slowly and with care to minimize disturbance or loss of fine-grained surficial sediment.

Once the overlying water has been removed, the top 2 cm of surficial sediment can be sub-sampled from the grab. Sub-samples are taken using a pre-cleaned flat bottom scoop. This device allows a relatively large sub-sample to be taken accurately. Because accurate and consistent subsampling requires practice, a trained and experienced person performs this task.

When subsampling surficial sediments, unrepresentative material (e.g., large stones or vegetative material) will be removed from the sample in the field. The smaller rocks and other small foreign material remain in the sample. The criteria used to determine representativeness of sample material will be established by the chief scientist prior to sub-sampling. Such removals will be noted on the field log sheet.

It is critical that sample contamination be avoided during sample collection. All sampling equipment (i.e., siphon hoses, scoops, containers) will be made of non-contaminating material and will be appropriately cleaned before use. Samples will not be touched with un-gloved fingers. In addition, potential airborne contamination (e.g., from engine exhaust, cigarette smoke) will be avoided.

3.7.2 Sediment sample collection utilizing diver cores

If water depth does not permit boat entrance to a site (e.g.. <8ft.), divers will sample that site using sediment cores (diver cores). Cores consist of a four-inch diameter polycarbonate tube, one-foot in length, including plastic end caps to aid in transport. A plunger covered with a plastic laboratory glove is used to extrude the mud for collection. All sample acceptability criteria will be met.

Divers will enter a study site from one end and sample in one direction so as to not disturb the sediment with feet or fins. Cores will be taken to a depth of at least six inches. Cores will be removed and a plunger will be placed on the bottom of the core. The sample will be extruded through the top of the core, allowing surface water to run off slowly, as stated for the grab sample procedure. The mud will be pressed out of the top end of the core to the prescribed depth of 2-cm and cut with a polycarbonate spatula, and will be deposited into the cleaned polyethylene tub. Additional samples will be taken with the same core tube until the six-liter volume is attained. Sediment samples will be treated similar to grab samples, with teflon sheets covering the sample and nitrogen vented.

Data sheets will be completed including latitude and longitude, salinity, temperature, etc., as outlined in Section 3.3.1. If sub-surface water samples are requested, they will be taken in an area of the site not yet disturbed by samplers.

If replicate samples are required, new core tubes will be used and new laboratory gloves will be placed over the plunger. Sampling will be conducted far enough apart to ensure no disturbance by the samplers during the previous replicate.

3.7.3 Transport of sample containers

Six-liter sample containers will be packed (three to an ice chest) with enough ice to keep them cool for 48 hours. Each tub will be sealed in two pre-cleaned, large plastic bags closed with a cable tie to prevent contact with other samples or ice or water. Ice chests will be driven back to the lab by the sampling crew or flown by air freight within 24 hours of collection.

3.8 HOMOGENIZATION AND ALIQUOTING OF SAMPLES

3.8.1 In-field sampling

For the sediment sample, the top 2-cm is removed from the grab and placed in the 6-liter polyethylene container. Between grabs or cores, the sediment in the container will be covered with a teflon sheet and the container covered with a lid and kept cool. When an adequate amount of sediment has been taken, the sample is covered with a teflon sheet assuring no air bubbles. A second, larger teflon sheet is placed over the top of the container to ensure an air tight seal, and nitrogen is vented into the container to rid it of oxygen.

3.8.2 In-laboratory homogenization and aliquoting

3.8.2.1 Homogenization

Samples will remain in ice chest (on ice, in double-wrapped plastic bags) until the containers are brought back to the lab for homogenization. All sample identification information (station numbers, etc.) will be recorded on COC and COR forms prior to homogenizing and aliquoting. A single container will be placed on plastic sheeting while also remaining in original plastic bags. The sample will be stirred with a polycarbonate stirring rod for at least 5 minutes, or until mud appears homogeneous.

3.8.2.2 Aliquoting and Storage

All pre-labeled jars will be filled using a clean teflon scoop, and will be stored in freezer/refrigerator (according to media/analysis) until analysis. Samples will be placed in boxes sorted by analysis type and leg number. The first sample taken is for **acid volatile sulfide (AVS)**,if authorized and funded. The remainder of the sediment sample is then aliquoted into appropriate containers for trace metal chemistry, organic chemistry, porewater extraction, and bioassay testing containers. The sample containers for sediment bioassays are then placed in a refrigerator (4°C). Sample containers for sediment chemistry (metals and organics) are stored in a freezer (-20°C). Any excess sediment sample will be archived in a clean ziplock bag placed in a refrigerator until the next leg.

3.8.2.3 Sample Storage Temperature and Holding Time

Sample storage temperatures and holding times are described in Section 5 of this QAPP.

3.9 PROCEDURES FOR THE EXTRACTION OF PORE WATER

3.9.1 Introduction

Simple pore water (interstitial water, or water which exists between sediments) extraction techniques can be used to collect and evaluate sediment pore waters during bio-geochemical and toxicological studies. These techniques are also necessary to determine pollutant profiles with sufficient resolution to model benthic fluxes. One method employed to extract pore water from sediment is centrifugation. Centrifuging may be used in this program at various times, and thus a brief description of the centrifugation method is given in Section 3.9.6.

The BPTCP has used whole core squeezing, primarily, to extract pore water. If funding is provided, a comparison of these methods will be performed in order to document any possible biases of each method (centrifuging and whole core squeezing). The whole core squeezing method, developed by Bender et al. (1987), utilizes mechanical force to squeeze pore water from interstitial spaces. It has been used for examination of nutrients and particle-unreactive ions in superficial sediments, with promising results. Tracer experiments and comparisons with other pore water extraction techniques agree favorably and support the

validity of this method. The following squeezing technique is a modification of the original Bender design with some adaptations based on the work of Carr et al.(1989) and Long and Buchman (1989). These modifications allow the squeezing technique to be useful in evaluating not only pollutant levels in pore waters of homogenized sediments, but could also allow profiling and determination of other important chemical redox characteristics in the sediments as well. This can be accomplished by whole core sampling and placing oxygen, pH or ion selective electrodes in-line with sample effluent during sample squeezing (Fairey et al., submitted).

3.9.2 Sediment sampling for whole core squeezer pore water extraction

The whole core squeezer (WCS) was developed for laboratory or field use in conjunction with standard coring techniques. It is most effective when used with coring devices which preserve the sediment-water interface and the overlying water, or by diver coring. When using coring devices, it is recommended that all surfaces in contact with sediment samples be manufactured or coated with non-contaminating surfaces (PPE, PEE or TFE) and be thoroughly cleaned (see section 6.0). Divers will minimize sample surface disturbance during sampling and also be aware of potential contamination problems.

3.9.3 Whole core squeezer instrument description

The squeezer's major features consist of an aluminum support framework, 10 cm i.d. acrylic core tubes with sampling ports, a pressure regulated pneumatic ram with air supply valves, and Ph and oxygen electrodes placed in-line with sample effluent. Subcore tubes are easily placed in the support framework by release of the coupler pin. Upon return to the framework, pressure is applied to the top piston by adjusting the air supply to the pneumatic ram. Initially an air pressure of $\approx$ 20 psi is sufficient to maintain a steady flow of sample effluent through the top piston. At no time during squeezing will air pressure exceed 200 psi. A porous pre-filter (PPE or TFE) is inserted in the top piston and used to screen large ($>$ 70 microns) sediment particles. Further filtration is accomplished with disposable TFE filters of 5 microns and 0.45 microns in-line with sample effluent. Filter clogging and sediment

compaction during the course of squeezing will slow effluent flow, so air pressure is slowly raised to compensate. This is easily accomplished with a fine adjustment pressure regulator on the air supply.

3.9.4 Whole core squeezer pore water sample extraction process and handling

To avoid trace metal contamination, all sample containers, filters and WCS surfaces in contact with the sample are plastics (acrylic, PVC, and TFE) and cleaned with Micro, 10% HCl, Type II--Milli-Q (brand) water--and methanol (see Section 3.6). One to two liters of homogenized sediment sample are placed in the squeezer tube for pore water extractions. Sample effluent of the required volume is collected in TFE containers under refrigeration. Pore water is then subsampled in the volumes and specific containers required for archiving, chemical or toxicological analysis. Samples to be analyzed for trace metals will be acidified to an approximate pH of 2-3 to minimize oxidation of the metal and adsorption to sample container walls. Other subsamples may be refrigerated or frozen as required under normal holding time criteria for each specific analysis. Upon completion of a sediment squeezing run, all squeezer surfaces in contact with sample will be thoroughly cleaned to minimize metal or organic cross-contamination between samples.

Blanks of Type II--Milli-Q (brand)-- water will be substituted for sample and squeezed prior to and after the core tubes are used for sample extractions. This squeezer blank will be used as a QC step to test for possible contaminations.

3.9.5 Documentation

As with any sampling, careful documentation is necessary. Comments relating to starting and ending time of a squeezing run, volumes squeezed and salinity of pore water will be recorded in the laboratory notebook. If in-line electrodes are being used, data relevant to their use will be logged or recorded on the strip chart.

3.9.6 Use of Centrifugation to Extract Pore Water

Although pore water extraction for the BPTCP has been primarily accomplished through the use of the whole core squeezing apparatus, centrifugation is also a scientifically valid method to extract porewater (Ankley et al, 1991a; Ankley et al, 1991b), and may also be utilized to extract pore water at times during this program. Sediment samples will be placed in cleaned one-liter polycarbonate centrifuge tubes, spun at 2,500 g for 30 minutes at 4°C in a Beckman J-6 refrigerated centrifuge. Four one-liter samples will be spun at a time.

3.10 COLLECTION OF SAMPLES FOR BENTHIC COMMUNITY ANALYSIS

The triangular sampling design (Section 3.2) can be used to collect a single replicate core from each of three predetermined stations with two additional samples taken randomly within the triangular pattern (n = 5). Although the location of the first three samples is not done by a formal randomization process, there is ample evidence (and no contrary evidence) that haphazard sampling of sediment communities does not differ from a formal random sampling design (Fager, 1972). Infaunal sediment cores are washed through screens with 0.5 mm openings to remove fine sediments. The screen residues are preserved in a 4% solution of formaldehyde to ensure specimen integrity. Organic stain, such as rose bengal, is not used as it distorts the natural coloration, which can be useful in taxonomic identification. After 3-4 days, samples are transferred to a 70% isopropyl alcohol solution, and stored for future sorting, taxonomy, and community analysis.

3.11 COLLECTION OF FISH SAMPLES

Fish may be used to examine contaminant information from particular areas. An initial screening of fish will be conducted in each region of the state for contaminant data, and to examine the possible use of fish for further BPTCP work. Fish will be captured using otter trawls, beach seines, gillnets, beam trawls, diver-deployed devices and other gear, as warranted by sample area: depth, accessibility, bottom-topography, and regulations and restrictions. Captured fish will be removed from the capture device and placed in a trace

metal-free and synthetic organic-free container for sorting. Captured fish will be sorted by species and size class, then rinsed with ambient water to remove sediments and debris. Two or more species groupings will be retained as possible samples. The fish will be individually packaged in doubled, pre-cleaned plastic bags (two bags) and frozen using dry ice in the field. Like-species fish will be individually weighed to arrive at a mean weight, standard deviation, and range, which will aide in choosing the most suitable species for chemical analysis. This section will be updated as necessary for more in-depth fish contaminant projects which may become a component of future BPTCP work. Other projects which are components of the BPTCP may involve the capture and use of live fish or shellfish for bioaccumulation or biomarker studies. These projects shall have stand-alone QAPP's.

3.12 SAMPLE COLLECTION AND STORAGE FOR AVS (acid volatile sulfide) ANALYSIS

Samples which will be utilized for AVS analysis will be taken from the top 2-cm of sediment from a box core (in the field) or from the homogenized sample in the laboratory. Plastic sample containers will be filled completely with sediment assuring no air spaces and kept on ice till freezing is possible. Samples will be held frozen for up to twelve months, unless otherwise recorded. Sample volatilization and extraction will be completed in accordance with Boothman, W.S. and Helmstetter, A. 1992. Sediment sulfides will be measured using a colorimetric method, suggested to be more accurate than the electrode method (Allen et al., 1991).

SECTION 3 (continued)

PART B: GENERAL LABORATORY OPERATIONS FOR ALL BPTCP LABS

3.13 LABORATORY OPERATIONS

This section addresses only general laboratory operations, while the sections on each biological indicator/laboratory component present specific QA/QC requirements and procedures associated with the processing of specific samples. All laboratories providing analytical support for chemical or biological analyses will have the appropriate facilities to store, prepare, and process 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 (where possible) logbooks, with all entries in ink.
- Monitoring and documenting the temperatures of cold storage areas and freezer units once per week.
- 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 will not exceed 18 megohm at 25° C.

- Labeling all containers used in the laboratory with date prepared, contents, and initials of the individual who prepared the contents; other information as appropriate.
- 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.
- QAPP, SOP's, analytical methods manuals, safety plans readily available to staff.

Laboratories will 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 will also be able to provide analytical data and associated QA/QC information in a format and time frame agreed upon with the DFG BPTCP Project Manager or designee.

3.13.1 Laboratory Personnel, Training and Safety

Each laboratory providing analytical support to BPTCP has a designated on-site QC Officer for the particular analytical component(s) performed at that lab (See Table 2-1). This individual will serve as the point of contact for the DFG BPTCP 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 will participate in an orientation session conducted during an initial site visit or via communications with DFG BPTCP staff. The purpose of the orientation session is to familiarize key laboratory personnel with the QAPP and the QA/QC program. Participating 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, and by participation in interlaboratory round-robin programs. Meetings shall be held with all participating laboratories at regular intervals to continually review QA/QC procedures, and to revise/update the QAPP.

Personnel in any laboratory performing BPTCP analyses will be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the particular analytical component project officer, laboratory manager and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. Each 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 will be readily available to laboratory personnel. Proper procedures for safe storage, handling and disposal of chemicals will be followed at all times; each chemical will be treated as a potential health hazard and good laboratory practices will be implemented accordingly.

3.13.2 Quality Assurance Documentation

All laboratories will have the latest revisions of the overall BPTCP QAPP. In addition, the following documents and information will be current, and they will be available to all laboratory personnel participating in the processing of BPTCP samples, as well as to DFG and SWRCB project officials:

- 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): Contains instructions for performing routine laboratory procedures, such as freezer logs, equipment and instrument instruction information, etc.

- Laboratory Analytical Methods Manual: Step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Contains all analytical methods utilized in the particular lab for the BPTCP.

- Instrument performance 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 will be developed and maintained throughout the project for all appropriate analyses and measurements (see section 3.2.5).

3.13.3 Analytical Procedures

Complete and detailed procedures for processing and analysis of samples in the field have been noted in previous portions of Section 3, and detailed procedures for processing and analysis of samples in the laboratory are provided in the respective laboratories Analytical Methods Manual.

3.13.4 Laboratory Performance Audits/Corrective Action

Initially, a QA performance audit will be performed by DFG BPTCP QA staff to determine if each laboratory effort is in compliance with the procedures outlined in the DFG QAPP and to assist the laboratory where needed. Additionally, technical systems audits will be conducted by a team composed of the DFG QA Officer or designee, and his/her technical assistants. Reviews may be conducted at any time during the scope of the study, but will occur no less than annually. Results will be reviewed with participating laboratory staffs and corrective action recommended and implemented, where necessary. Furthermore, laboratory performance will be assessed on a continuous basis through the use of laboratory intercomparison studies (round robins). Laboratories performing organic and metal chemistry analyses will be required to participate in the annual National Status and Trends Intercalibration, and to report the findings to DFG BPTCP Project Manager, or his/her designee, and the DFG QA Officer.

3.13.5 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).

Measured values are plotted in their sequence of measurement. Three sets of limits are superimposed on the chart: 1) the "central line", 2) the upper and lower "warning limits", and 3) the upper and lower "control limits". These values are listed in Table 5.3.

Control charts will 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 will be taken (Taylor 1987):

- If the measured value of the control sample is within the warning limits as shown in Table 5.3, 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 will 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 as shown in Table 5.3, 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 will 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.

Central line, warning limits, and control limits will be evaluated periodically by either the on-site Laboratory QC coordinator or the DFG BPTCP 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 will be available for review during technical systems audits. Copies of charts will be furnished to the DFG BPTCP QA staff upon request, and shall be submitted routinely as a component of QA/QC reports to DFG BPTCP staff. Such charts will contain both the points and their associated values.

SECTION 4

QUALITY ASSURANCE OBJECTIVES

4.1 MEASUREMENT QUALITY OBJECTIVES

The BPTCP is measuring a defined set of parameters that are considered to be reliable indicators of bay and estuarine environmental condition. Table 4.1 lists the indicators measured in this program. Additional indicators being evaluated for possible inclusion are contaminant concentrations in fish tissue, biomarkers in fish and mussels, and various other habitat indicators (redox potential discontinuity depth, secchi depth, temperature and salinity stratification profiles, dissolved oxygen, pH, and possibly other parameters).

TABLE 4-1. Indicators measured in the BPTCP.

Category	Indicator
Biotic Condition	Benthic species composition
Abiotic Condition	Sediment contaminant concentrations
	Sediment, pore water and subsurface water toxicity
	TOC
	Ammonia
	H_2S
Habitat	Salinity
	Temperature
	Depth
	Grain size

Measurement error is frequently emphasized in monitoring programs as an important source of uncertainty. In the BPTCP, 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 BPTCP data may find that measurement error is an important source of variability that will be accounted for. It is therefore important for the BPTCP laboratories and field crews to control measurement error, to the extent possible, when selecting sampling methods and establishing measurement quality objectives (MQO's) for each sampling method and laboratory analysis procedure. MQO's 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.

Measurement quality objectives for the various measurements being made in the BPTCP are expressed in terms of accuracy, precision, and completeness requirements in Table 4-2. These MQO's 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 MQO's presented in Table 4-2 are used as quality control criteria both in field and laboratory measurement processes to set the bounds of acceptable measurement error. Usually, MQO's are established for five aspects of data quality: representativeness, completeness, comparability, accuracy, and precision (Stanley and Verner 1985, EPA 1988). These terms are described in the following sections in terms of their overall applicability to the BPTCP and the specific measurement systems being employed for each indicator.

TABLE 4-2. Measurement quality objectives for BPTCP indicators. Accuracy 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 Requirement	Precision Requirement	Completeness Goal
Sediment/tissue contaminant analyses:			
Organics	30%	30%	95%
Inorganics	15%	30%	95%
Sediment toxicity	NA	NA	95%
Benthic species composition and biomass:			
Sorting	10%	NA	95%
Counting	10%	NA	95%
Taxonomy	10%	NA	95%
Sediment characteristics:			
Particle size (% silt-clay) analysis	NA	10%	95%
Total organic carbon	10%	10%	95%
Acid volatile sulfide	**10%**	**10%**	**95%**
Water Column Characteristics:			
Dissolved oxygen	± 0.5 mg/L	10%	95%
Salinity	± 1.0 ppt	10%	95%
Depth	± 0.5 m	10%	95%
pH	± 0.2 units	NA	95%
Temperature	± 0.5 °C	NA	95%
Total Suspended solids	NA	10%	95%
Gross pathology of fish	NA	10%	95%
Fish community composition:			
Counting	10%	NA	95%
Taxonomic identification	10%	NA	95%
Length determinations	± 5 mm	NA	95%
Fish histopathology	NA	NA	NA

4.2 REPRESENTATIVENESS

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 the BPTCP'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 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). For the tests that the SWRCB directs to be performed, the BPTCP has established a completeness goal of 95% for the various indicators being measured (Table 4-3). The 95% completeness goal is established in an attempt to provide a comprehensive set of data for each site evaluated for toxic hot spot or reference site status. Failure to achieve this goal usually results from lost or destroyed samples. Therefore, established protocols for tracking samples during shipment and laboratory processing will 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 will be assured if the overall goals of the BPTCP are to be realized. One goal of the BPTCP is to generate a high level of documentation for the above topics to ensure that future BPTCP efforts can be made comparable. For example, both field and laboratory methods are described in full detail in field and analytical methods manuals which will be made available to all field personnel and analytical laboratories. Field crews will undergo training prior to the start of field work. Likewise, laboratory crews will be certified as trained to conduct the particular analyses and duties which they perform for the BPTCP. In addition, the comparability of laboratory measurements can be monitored through the interlaboratory comparison exercises **and the use of field split blind samples or laboratory duplicate samples**, if authorized and funded. The results of this comparability 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, 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 4-2). 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 because "true" or expected values do not exist for these measurement parameters (see Table 4-2). 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 4-3 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 4-3. 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.

4.6 COMPATIBILITY WITH PROGRAM GOALS

Presently, the BPTCP's primary purpose is the identification of Toxic Hot Spots, including the demonstration of an association with anthropogenic pollution (i.e. evidence, in the form of a statistical association, has to be presented that contaminants rather than natural factors such as grain size and ammonia are responsible for the observed toxicity or benthic degradation). Achieving this goal requires careful selection of nondegraded reference sites that match suspect hot spots for these natural factors. Presently, reference sites must generally be chosen which have been demonstrated to be nontoxic in repeat testing, which are matched with suspect hot spots for grain size and TOC, and which are located in the same geographic region (San Francisco Bay area or north or south of Pt. Conception). Later editions of this document will present the statistical tests used to determine whether the

association with contaminants exists independent of the effects of natural factors. Additional details will also be provided regarding the addition of benthic data, the process for selecting reference sites, reference site selection criteria, and statistical issues concerning the numbers and types of reference sites to be included in each attempt to qualify a group of sites as hot spots.

As later editions of this document address the program's additional goals of developing sediment quality objectives and remediating hot spots, this section will be supplemented with the appropriate quality assurance objectives to achieve compatibility with these goals.

TABLE 4-3. Quality assurance sample types, frequency of use, and types of data generated for BPTCP 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
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**

Table 4-3 (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 BPTCP's 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 the SWRCB Mussel Watch program, 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 (see Table 5-4). This guidance is applicable to low parts per billion analyses of both estuarine sediment and tissue samples unless otherwise noted. Detailed descriptions of the analytical techniques and laboratory standard operating procedures are reported elsewhere (DFG, 1992).

The BPTCP measures a variety of organic and inorganic contaminants in estuarine sediment and fish tissue samples (Table 5-1); these compounds include all those measured in the NOAA NS&T Program. The BPTCP 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

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[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 the BPTCP and their detection limits in sediments and tissue.

CHEMICAL ANALYSES REGULARLY PERFORMED FOR BPTCP

POLYCYCLIC AROMATIC HYDROCARBONS (PAH's):

Analyte	Detection Limit (ng/g dry)	
	Sediment	Tissue
Naphthalene	5	10
2-Methylnaphthalene	5	10
1-Methylnaphthalene	5	10
Biphenyl	5	10
2,6-Dimethylnaphthalene	5	10
Acenaphthylene	5	10
Acenaphthene	5	10
2,3,5-Trimethylnaphthalene	5	10
Fluorene	5	10
Dibenzothiophene	5	10
Phenanthrene	5	10
Anthracene	5	10
1-Methylphenanthrene	5	10
Fluoranthrene	5	10
Pyrene	5	10
Benz[a]anthracene	5	10
Chrysene	5	10
Benzo[b]fluoranthrene	5	10
Benzo[k]fluoranthrene	5	10
Benzo[e]pyrene	5	10
Benzo[a]pyrene	5	10
Perylene	10	15
Indo[1,2,3-cd]pyrene	10	15
Dibenz[a,h]anthracene	10	15
Benzo[ghi]perylene	5	10

DDT AND ITS METABOLITES:

Analyte	Detection Limit (ng/g dry)	
	Sediment	Tissue
o,p'-DDD	1	5
p,p'-DDD	0.4	3
o,p'-DDE	1	3
p,p'-DDE	1	1
o,p'-DDT	1	4
p,p'-DDT	1	4
p,p'-DDMS	3	20
p,p'-DDMU	2	5

CHLORINATED ORGANIC PESTICIDES OTHER THAN DDT:

Analyte	Detection Limit (ng/g dry)	
	Sediment	Tissue
Aldrin	0.5	1
Endrin	2	6
alpha-Chlordene	0.5	1
Endosulfan I	0.5	1
trans-Nonachlor	0.5	1
Dieldrin	0.5	1
Heptachlor	0.5	1
Heptachlor Epoxide	0.5	1
Hexachlorobenzene	0.2	1
gamma-HCH	0.2	0.8
Mirex	0.5	1
cis-Chlordane	0.5	1
trans-Chlordane	0.5	1
gamma-Chlordene	0.5	1
Chlorpyrifos	1	4
Dacthal	0.2	2
p,p'-Dichlorobenzophenone	3	25
Endosulfan II	1.0	3
Endosulfan sulfate	2	5
alpha-HCH	0.2	1

CHLORINATED ORGANIC PESTICIDES OTHER THAN DDT (Continued):

Analyte	Detection Limit (ng/g dry)	
beta-HCH	1	3
delta-HCH	0.5	2
Methoxychlor	1.5	15
cis-Nonachlor	0.5	1
Oxadiazon*	2	6
Oxychlordane	0.5	1
Toxaphene	10	100

*Not routinely analyzed, additional costs

NIST PCB CONGENERS:

Analyte	Detection Limit (ng/g dry)	
	Sediment	Tissue
2,4'-dichlorobiphenyl PCB 8	0.5	1
2,2',5-trichlorobiphenyl PCB 18	0.5	1
2,4,4'-trichlorobiphenyl PCB 28	0.5	1
2,2',3,5'-tetrachlorobiphenyl PCB 44	0.5	1
2,2',5,5'-tetrachlorobiphenyl PCB 52	0.5	1
2,3',4,4'-tetrachlorobiphenyl PCB 66	0.5	1
2,2',4,5,5'-pentachlorobiphenyl PCB 101	0.5	1
2,3,3',4,4'-pentachlorobiphenyl PCB 105	0.5	1
2,3',4,4',5-pentachlorobiphenyl PCB 118	0.5	1
2,2',3,3',4,4'-hexachlorobiphenyl PCB 128	0.5	1
2,2',3,4,4',5'-hexachlorobiphenyl PCB 138	0.5	1
2,2',4,4',5,5'-hexachlorobiphenyl PCB 153	0.5	1
2,2',3,3',4,4',5-heptachlorobiphenyl PCB 170	0.5	1
2,2',3,4,4',5,5'-heptachlorobiphenyl PCB 180	0.5	1
2,2',3,4',5,5',6-heptachlorobiphenyl PCB 187	0.5	1
2,2',3,3',4,4',5,6-octachlorobiphenyl PCB 195	0.5	1
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl PCB 206	0.5	1
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl PCB 209	0.5	1

ORGANOMETALIC COMPOUNDS:

Tributyltin	13 ng/g	20 ng/g

TRACE ELEMENTS: NOTE: Values for trace elements are micrograms/gram (ppm)

Element	Detection Limit (ug/g dry)	
	Sediment	Tissue
Aluminum	1	1
Antimony	0.1	0.1
Arsenic	0.1*	0.25
Cadmium	0.01	0.01
Chromium	0.1	0.1
Copper	0.1	0.1
Iron	0.1	0.1
Lead	0.1	0.1
Manganese	0.05	0.05
Mercury	0.03	0.03
Nickel	0.1	0.1
*Selenium	0.2*	0.1
Silver	0.01	0.01
Tin	0.02	0.02
Zinc	0.05	0.05

*denotes that for Arsenic and Selenium, an average percent moisture value is used for establishing these detection limits, with 50% moisture in sediments and 80% in tissue.

ADDITIONAL ANALYSES WHICH CAN BE PERFORMED IF AUTHORIZED
(not presently part of the regular suite of BPTCP chemical analyses)

ADDITIONAL PCB CONGENERS:

Analyte	Detection Limit (ng/g dry)	
	Sediment	Tissue
2,3-dichlorobiphenyl PCB 5	0.5	1
4,4'-dichlorobiphenyl PCB 15	0.5	1
2,3',6-trichlorobiphenyl PCB 27	0.5	1
2,4,5-trichlorobiphenyl PCB 29	0.5	1
2,4',4-trichlorobiphenyl PCB 31	0.5	1
2,2,'4,5'-tetrachlorobiphenyl PCB 49	0.5	1
2,3',4',5-tetrachlorobiphenyl PCB 70	0.5	1
2,4,4',5-tetrachlorobiphenyl PCB 74	0.5	1

ADDITIONAL PCB CONGENERS (Continued):

Analyte	Detection Limit (ng/g dry)	
	Sediment	Tissue
2,2',3,5',6-pentachlorobiphenyl PCB 95	0.5	1
2,2',3',4,5-pentachlorobiphenyl PCB 97	0.5	1
2,2',4,4',5-pentachlorobiphenyl PCB 99	0.5	1
2,3,3',4',6-pentachlorobiphenyl PCB 110	0.5	1
2,2',3,3',4,6'-hexachlorobiphenyl PCB 132	0.5	1
2,2',3,4,4',5-hexachlorobiphenyl PCB 137	0.5	1
2,2',3,4',5',6-hexachlorobiphenyl PCB 149	0.5	1
2,2',3,5,5',6-hexachlorobiphenyl PCB 151	0.5	1
2,3,3',4,4',5-hexachlorobiphenyl PCB 156	0.5	1
2,3,3',4,4',5'-hexachlorobiphenyl PCB 157	0.5	1
2,3,3',4,4',6-hexachlorobiphenyl PCB 158	0.5	1
2,2',3,3',4,5,6'-heptachlorobiphenyl PCB 174	0.5	1
2,2',3,3',4',5,6-heptachlorobiphenyl PCB 177	0.5	1
2,2',3,4,4',5',6-heptachlorobiphenyl PCB 183	0.5	1
2,3,3',4,4',5,5'-heptachlorobiphenyl PCB 189	0.5	1
2,2',3,3',4,4',5,5'-octachlorobiphenyl PCB 194	0.5	1
2,2',3,3',4,5',6,6'-octachlorobiphenyl PCB 201	0.5	1
2,2',3,4,4',5,5',6-octachlorobiphenyl PCB 203	0.5	1

Additional chemical analyses that can be performed, if funded and authorized:

a) Terphenyl
b) Quantifying unknown chromatography peaks
c) Pthalates
c) Acid volatile sulfide (on sediment)

exercises (round-robins). This is a "performance-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 duplicated blind samples**, if authorized and funded. 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 BPTCP are those used in the NOAA NS&T Program (Lauenstein et al. 1993), as well as those documented in the DFG QAQC Manual (DFG, 1992). Under the BPTCP 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 will, 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 will strictly adhere to the BPTCP protocols to insure the collection of representative, uncontaminated sediment and fish tissue chemistry samples. These sample collection protocols are described in detail in this document (see Section 3). Briefly, the key aspects of quality control associated with chemistry sample collection are as follows: 1) field personnel will be thoroughly trained in the proper use of sample collection gear and will be able to distinguish acceptable versus unacceptable sediment grab samples or fish trawls in accordance with pre-established criteria, 2) field personnel will 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 will be made of non-contaminating materials (e.g., glass, high-quality stainless steel and/or Teflon®) and will be thoroughly cleaned between sampling stations, 4) sample containers will be of the recommended type (Table 5-2) and will be free of contaminants (i.e., carefully pre-cleaned), and 5) conditions for sample collection, preservation and holding times will be followed (Table 5-2).

Table 5-2. Summary of chemistry sample collection, preservation, and holding time conditions to be followed for BPTCP monitoring.

Sample Parameter	Sample Container	Sample Volume	Max. Sample Size	Holding Temperature	Max. Sample Hold Time[b]	Max. Extract Holding Time
Sediment Metals (except Hg)	250-ml HDPE wide mouth jar	100 to 150 ml	100 to 150 g (approx.)	Freeze, -18° 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	40 days
Sediment Acid Volatile Sulfide (AVS)	**125-ml poly propylene wide-mouth jar**	**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)	1.5 years[d]	40 days

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

[b] Every effort will be made to analyze these samples as soon as possible. If extractions are not to be performed within 14 days (or 28 days with Mercury), these samples will be frozen (-18°C) and extracted within 1.5 years.

[c] AVS containers will be filled to the top to minimize or eliminate headspace; containers will be capped tightly. Every effort will 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 will always be followed, as long as the minimum requirements presented in this document have been met.

The performance-based protocols utilized in the BPTCP 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 initial analysis of samples, each laboratory will demonstrate proficiency in several ways: written protocols for the analytical methods to be employed for sample analysis will be submitted to the Program for review, method detection limits for each analyte will be calculated, an initial calibration curve will be established for all analytes, and acceptable performance will be shown on a known or blind accuracy-based material. Following a successful first phase, the laboratory will 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 5-3. The sections are arranged to mirror the elements in Table 5-3 to provide easy cross-reference for the reader.

The results for the various QA/QC samples will be reviewed by laboratory personnel immediately following the analysis of each sample batch. These results then will be used to

determine when warning and control limit criteria have not been met and corrective actions will 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 BPTCP also are summarized in Table 5-3.

Table 5-4 provides a list of references for analytical procedures utilized for chemical analyses conducted in the BPTCP.

TABLE 5-3. Key elements of laboratory quality control for BPTCP 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 5-1)		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	At least once each year
- Continuing Calibration Checks using Calibration Standard Solutions	NA	will 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

TABLE 5-3 (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 to be within 3sd of control chart limits	Value plotted on control chart after each analysis of the CRM
Relative Accuracy (see NOTE 2):			
PAHs	Lab's value will 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 will 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 will be within ±15% of true value for each analyte	Lab will be within ±20% of true value for each analyte	

NOTE 1: The use of control charts to monitor precision for each analyte of interest will 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, will 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 will 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.

TABLE 5-3 (continued).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
- Laboratory Reagent Blank	Analysts will use best professional judgement if analytes are detected at <3 times the MDL	No analyte will be detected at >3 times the MDL	One with each batch of samples
- Internal Standards (Surrogates)	NA	Recovery will be within the range 30% to 150%	Each sample
- Injection Internal Standards	Lab develops its own	Lab develops its own	Each sample
The following procedures can be performed, if authorized and funded:			
- Laboratory Fortified Sample Matrix (Matrix Spike)	**NA**	**Recovery try to be within the range 50% to 120% for at least 80% of the analytes**	**At least 5% of total number of samples**
- Laboratory Fortified Sample Matrix Duplicate (Mat. Spike Dup.)	**NA**	**RPD[1] will be ≤ 30 for each analyte**	**Same as matrix spike**
- Field Duplicates (Field Splits)	**NA**	**RPD[1] will be ≤ 30 for each analyte**	**5% of total number of samples**

NOTE: Samples to be spiked will be chosen at random; matrix spike solutions will contain all the analytes of interest. The final spiked concentration of each analyte in the sample will be at least 10 times the calculated MDL.

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

Table 5-4: References for analytical methods utilized for chemical analyses conducted in the BPTCP.

Trace Metal Chemistry:

*Evans, D. and P. Hanson. 1993. Analytical methods for trace elements in sediments by atomic absorption spectrophotometry. In Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Project 1984-1992, vol. 3. Lauenstein, G. and A. Cantillo (eds.). NOAA Tech. Mem. NOS ORCA 71, p. 53-81.

Selenium:

California Department of Fish and Game, Water Pollution Control Laboratory Standard Operating Procedure for the Determination of Selenium in Biological Tissue, Sediment, and Water. 1990.

Arsenic:

California Department of Fish and Game, Water Pollution Control Laboratory Standard Operating Procedure for the Determination of Arsenic in Biological Tissue, Sediment, and Water. 1990.

Organic Chemistry:

*MacLeod, W, D. Brown, A. Friedman, D. Burrows, O. Maynes, R. Pearce, C. Wilgren, and R. Bogar. 1993. Standard analytical procedures of the NOAA national analytical facility, 1985-1986. In Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Project 1984-1992, vol. 4. G. Lauenstein and A. Cantillo (eds.). NOAA Tech. Mem. NOS ORCA 71, p.1-50.

Acid volatile sulfides (AVS):

*Boothman, W. and A. Helmstetter. 1992. Determination of acid-volatile sulfide and simultaneously extracted metals in sediment using sulfide-specific electrode detection. unpubl. 12p.

Table 5-4 (Continued)

Unionized Ammonia:

APHA. 1985. Standard Methods for the Examination of Water and Wastewater. 16th ed. American Public Health Association, Washington D.C. 1268p.

Khoo, K., C. Culberson, and R. Bates. 1977. Thermodynamics of dissociation of ammonium ion in seawater from 5 to 40 C. Journal of Solution Chemistry 6:281-290.

Hydrogen Sulfide:

Fonselius, S. 1985. Determination of hydrogen sulfide. in Methods of seawater analysis. K. Grasshoff, M. Ehrhardt, and K. Kremling (eds.) 2nd ed.

Savenko, V. 1977. Marine Chemistry: the dissociation of hydrogen sulfide in seawater. Oceanology 16:347-350.

Total Organic Carbon:

Stephenson, M., M.Puckett, N. Morgan, and M. Reid. 1994. Quality Assurance Project Plan for the Bay Protection and Toxic Cleanup Program. Section 9.

Control Equipment Corporation. 1990. Elemental Analyzer Manual

Grain Size:

*Folk, R. 1974 Petrology of Sedimentary Rocks. Hemphill Publ. Co., Austin, Tx. 182p.

Tributyltin:

Stephenson, M. and D. Smith. 1988. Determination of tributyltin in tissues and sediment by graphite furnace atomic absorption spectrophometer. Analytical Chemistry 60(7):696-698.

* denotes that cited methods have been modified for the BPTCP analyses.

5.3.2 Initial Demonstration of Capability

5.3.2.1 Instrument Calibration

Equipment will 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 5-3). All calibration standards will 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 will 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 will be well-characterized and will 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 will be diluted or concentrated, as appropriate, and reanalyzed.

5.3.2.2 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 BPTCP, 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 BPTCP analytical laboratory will 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 will 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 BPTCP (See Table 5-1). The initial MDLs reported by each laboratory will be equal to or less than these specified target values before the analysis of field samples may proceed. Each laboratory will periodically (*i.e.*, at least once each year) re-evaluate its MDLs for the analytical methods used and the sample matrices typically encountered.

5.3.2.3 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 BPTCP; 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 NS&T 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

5.3.3.1 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 the BPTCP analytical laboratories are required to participate in intercalibration 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 BPTCP 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, one exercise is 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 will submit their results in a timely manner both to the BPTCP 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 requested to participate in the annual QA workshops, which provide a forum for discussion of analytical problems brought to light in the comparison exercises.

5.3.3.2 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 BPTCP laboratories is presented in Table 5-5.

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

Table 5-5. Certified Reference Materials commonly used by BPTCP 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

among different laboratories. If available, LCMs may be preferred for routine (*i.e.*, day to day) analysis because CRMs are relatively expensive.

Routine analysis of Certified Reference Materials or, when available, Laboratory Control Materials represents a particularly vital aspect of the "performance-based" BPTCP QA philosophy. At least one CRM or LCM must be analyzed along with each batch of 25 or fewer samples (Table 5-3). For CRMs, both the certified and non-certified concentrations of the target analytes will be known to the analyst(s) and will 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 5-3); 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 will 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 will 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) will be updated annually; 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 >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 BPTCP 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 as described in Table 5-3.

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 5-3). 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 will be within $<30\%$ of the true value on average for each combined group of organic compounds, and the laboratory's value will 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 will 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.

5.3.3.3 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 will contain all the analytes of interest. At a minimum, analysis of the calibration check solution will occur at the start and at the end of each sample batch. Analysts will 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 5-3), the initial calibration will have to be repeated. If possible, the samples analyzed before the calibration check sample that failed the control limit criteria will be reanalyzed following the recalibration. The laboratory will 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 will 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 will 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 will prepare a narrative explanation to accompany the submitted data.

5.3.3.4 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 will be run in every sample batch. The reagent blank will be processed through the entire analytical procedure in a manner identical to the samples. Warning and control limits for blanks (Table 5-3) 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 will 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.

5.3.3.5 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 is adjusted to correct for the recovery of the internal standard, as done in the NOAA National Status and Trends Program. The internal standard recovery data therefore will 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 will be used as internal standards.

Control limit criteria for internal standard recoveries are provided in Table 5-3. Each laboratory will 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).

5.3.3.6 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 will be different from those already used as internal standards. The analyst(s) will monitor injection internal standard retention times and recoveries to determine if instrument maintenance or repair, or changes in analytical procedures, are indicated. Corrective action will 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 will be documented properly in logbooks and internal data reports and used by the laboratory personnel to take appropriate corrective action.

5.3.3.7 Laboratory Duplicates for Precision

A minimum of 5% of the total number of samples submitted to the laboratory in a given year will be selected at random for analysis as laboratory duplicates for precision. Analysis of laboratory duplicates is useful for assessing laboratory precision. The relative percent difference (RPD) between the 2 duplicate sample results will be less than 30 for each analyte of interest (see Table 5-3). 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 $< 30\%$ control limit criteria, calculations and instruments will 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.

5.3.3.8 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, if authorized and funded. A minimum of 5% of the total number of samples submitted to the laboratory in a given year will 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 will contain all the analytes of interest. The final spiked concentration of each analyte in the sample will 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 will 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 will be discussed in a cover letter accompanying the data package. Corrective actions taken and verification of acceptable instrument response will 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 will be less than 30 for each analyte of interest (see Table 5-1). 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 < 30% control limit criteria, calculations and instruments will 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.

5.3.3.9 Field Duplicates and Field Splits

For the BPTCP, 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. One blind sample will be collected per leg for analysis, if authorized and funded.

5.4 OTHER SEDIMENT CHEMICAL 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, the BPTCP laboratories are required to measure several ancillary sediment chemical parameters, such as

total organic carbon (TOC), and tributyltin (TBT) concentrations, **and acid volatile sulfides (AVS), if authorized and funded.** The laboratory QA/QC requirements associated with tributyltin (TBT) and **acid volatile sulfides (AVS), if authorized and funded,** are presented in the following sections. Section 9 of this QAPP contains all pertinent information on total organic carbon (TOC) measurements and associated QA/QC requirements.

5.4.1 Tributyltin

Assessment of the distribution and environmental impact of tributyltin requires its 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 will 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) will be analyzed along with each batch of 25 or fewer samples to evaluate the recovery of the butyltin species of interest, if authorized and funded. The butyltins will 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 will 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 will 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 will 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.

5.4.2 Acid Volatile Sulfide

Note: This analysis is currently not conducted as a part of the BPTCP, but will be performed if authorized and funded. Quality control of acid volatile sulfide (AVS) measurements is achieved through the routine analysis of a variety of QA/QC samples. 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 will 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 will be less than 20%. If the RPD exceeds 20%, a third analysis will be performed. If the relative standard deviation of the three determined concentrations exceeds 20%, the individual analyses will be examined to determine if non-random errors may have occurred. As previously discussed, field duplicates will also be collected for AVS determination to assess 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 will 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) will 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 will be evaluated for sources of error and the analysis will be repeated. If recovery remains unacceptable, it is possible that matrix interferences are occurring. If possible, the analysis will 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) will 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.

5.5 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

5.5.1 Sample Tracking

BPTCP sample collection personnel have developed a comprehensive system for recording sampling information in the field and tracking sample shipments. 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 Data Librarian, as well as the particular laboratory project officer.

Laboratory personnel will be aware of the required sample holding times and conditions (see Table 5-2), 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 will verify that the measurement process was "in control" (i.e., all specified QA/QC requirements were met or acceptable deviations explained) for each batch of samples before proceeding with the analysis of a subsequent batch. In addition, each laboratory will 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, or data which has acceptable deviations explained, will be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable.

As stated in Section 3.3.4, "Authorization/Instructions to Process Samples" forms will be provided to each laboratory every time it receives a batch of samples for analysis. These forms are completed by DFG personnel, or its authorized designee, and are signed and accepted by both the DFG authorized staff and the staff accepting the samples on behalf of the particular laboratory. The forms contain all pertinent information necessary for the laboratory to process the samples, such as the exact type and number of tests to run, number of laboratory replicates, dilutions, exact eligible cost, deliverable products (including hard and soft copy specifications and formats), filenames for soft copy files, expected date of submission of deliverable products to DFG, and other information specific to the lab/analyses being performed.

Each chemistry data report package submitted to DFG will consist of at least the following, (specifically described requirements will be contained in "Authorization/Instructions to Process Samples" forms for each batch transferred, as described above):

- A cover letter transmitting the data report, and
- Text, 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, and

- Tabulated results (actual chemical data) in hard copy form, including % moisture, mass extracted, and concentrations of the analytes of interest (reported in units identified to three significant figures unless otherwise justified). Concentration units will be ng/g or ug/g (dry weight) for sediment or tissue. All data will be double entered or double verified to check for accuracy. A "Data Transmittal/Data Accuracy Verification" form will accompany the data report (and other required items as herein described and as required with specific "Authorization/Instructions to Process Samples" form for the particular batch), and the form will be signed by the laboratory's BPTCP project officer or designee. The data shall conform to the approved BPTCP Data Base Description. One unbound, one-sided original master for making copies, and two bound copies, will be submitted to DFG with each report, and

- Tabulated results in computer-readable form (e.g., 3.5" diskette, DOS format) included in the same shipment as the hard copy data, but packaged in a diskette mailer to prevent damage. The analytical data will be submitted to the DFG Data QC Officer in dBASE 4 format as outlined in the Database Description. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted, and

- Tabulated method detection limits achieved for the samples, with a verification of this in writing (an MDL chart), or an explanation for any acceptable deviations. This should be described and presented in the QA/QC Report that accompanies the data and is further described below, and

- QA/QC Report, in both hard copy (one unbound, one-sided original for duplicating; two bound copies) and soft copy (3.5" computer diskette in a diskette mailer). This QA/QC report will evaluate the data by analyzing the results for all QA/QC samples (*e.g.*, CRMs, calibration check samples, blanks, **matrix spike/matrix spike duplicates**, laboratory duplicates, etc.), and must be submitted by the analytical laboratory as part of the data package for each batch of samples analyzed. The laboratory is expected to provide a detailed explanation of any factors affecting data quality or interpretation. The laboratory submitting the data 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 batch number is described in the Data Base Description and is a field in the dBase database. Each type of analysis (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analyses, TOC and grain size, and **AVS, if authorized and funded**) will have a unique batch number. In addition to the batch number field, another field (metadata) will be included in all data sets (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analyses, TOC and grain size analysis, and **AVS, if authorized and funded**) which lists the file names that contain the summarized QC data and any text describing the data for that sample. The metadata field is described in the database description and will be entered into each of the data sets by each of the laboratories, and

- Any other required elements, as specified in "Authorization/Instructions to Process Samples" form for a particular batch.

Chemistry laboratories are responsible for assigning only two data codes ("-8" and "-9") to the submitted data. If an analysis was performed on a sample for a particular analyte, but the analyte is not detected, the laboratory will report the result as "-8", meaning "not detected". If a particular sample was not analyzed for a specific analyte for any reason, the laboratory will report the data for that sample and analyte as "-9", meaning "not analyzed". Some possible reasons a sample might not be analyzed: the sample was not authorized to have chemistry run on it; the sample was contaminated and the analysis could not be performed; the sample jar broke, and thus the sample was not usable; the sample was lost for any reason; etc.

TABLE 5-6. 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	ug/g or ng/g dry wt.
LCMPR	Lab Control Material % Recovery	Percent Recovery
LF1	**Lab Spiked Sample- 1st Member**	**ug/g or ng/g dry wt.**
LF1PR	**Lab Spiked Sample- 1st Mem. % Rec.**	**Percent Recovery**
LF2	**Lab Spiked Sample- 2nd Member**	**ug/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
MDL	Method Detection Limit	ug/g or ng/g dry wt.
FB	**Field Blank**	**ug/g or ng/g dry wt.**
FR	**Field Replicate**	**ug/g or ng/g dry wt.**

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 QA/QC tables are

referenced in the data base containing the data for the program in a separate field. Each sample will have a separate entry (stored in the main database as a separate field) that links it to the QA/QC summary database files for that sample.

5.5.3 Data Evaluation Procedures

It is the responsibility of the Data Librarian to acknowledge to the DFG Data QC Officer the initial receipt of the data package(s). It is then the responsibility of the DFG Data QC Officer and his/her designees to verify that the four data evaluation steps identified in the following paragraph are completed, and to subsequently notify the analytical laboratory of any additional information or corrective actions deemed necessary. A "Data Revision/Correction" form will be completed every time any data is revised, once data has been submitted to DFG. This form will accompany any revised data files, and will explain exactly what changes were made to the dataset. Following satisfactory resolution of all "corrective action" issues, the DFG BPTCP Data QC Officer will ask the DFG BPTCP Project Coordinator to 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. This will be accomplished by the use of a "Deliverable Product Acceptance Certification" form, to be signed by the DFG BPTCP Project Manager, DFG BPTCP Project Coordinator, DFG BPTCP Data QC Officer, with countersignature accepting the certification by the laboratory submitting the data package. A team of individuals (e.g., the DFG BPTCP QA Officer, DFG BPTCP Project Manager, DFG BPTCP Project Coordinator, DFG BPTCP Data QC Officer, SJSUF QC Officer, Data Librarian, and/or analytical chemists) to assist in technical evaluation of the submitted data packages. While the DFG BPTCP Project Coordinator 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 DFG BPTCP Data QC Officer to closely monitor and formally document each step in the process as it is completed. This documentation will be in the form of a "data evaluation tracking form and checklist" that is filled in as each step is completed. This checklist will be supplemented with detailed memos and any other

pertinent forms as previously described, to the project file outlining any concerns with data omissions, analysis problems, or descriptions of questionable data identified by the submitting laboratory or the DFG team.

Evaluation of the data package will 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 BPTCP chemistry data:

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

5.5.3.1 Checking Data Completeness

The first part of data evaluation is to verify that all required information has been provided in the data package. The steps to be followed in the assessment and evaluation of BPTCP chemistry data will be in accordance with EPA procedures (U.S. EPA, 1991). In the BPTCP, this will include the following specific steps:

- Project coordinator will verify that the package contains the information as outlined in Section 3.3.4, including, but not limited to the following: cover letter signed by the laboratory BPTCP project officer transmitting the data and QA/QC report package; narrative explanation (text) signed by the laboratory manager, hard copies of all results (including QA/QC results), and accompanying computer diskettes.

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

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

The DFG BPTCP Data QC Officer or his/her designee will 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 will provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

5.5.3.2 Assessing Data Quality

Data validation, or the process of assessing data quality, can begin after BPTCP 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, BPTCP laboratories are expected to submit data which already has been tabulated and checked 100% for accuracy (by double entry or verification), and the raw data reports needed by BPTCP 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 BPTCP 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 BPTCP 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, if authorized and funded**) 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 in BPTCP samples (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. If anomalous 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 will be tabulated, summarized and evaluated. Specifically, a set of summary tables will be prepared from the BPTCP database showing the **percent recovery values** and relative percent difference values (where applicable) for the following QA/QC samples: continuing calibration check samples, laboratory control material(s), and **matrix spike/matrix spike duplicate samples.** The tables will 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. These QA data tables are to be submitted in a dBase format or spreadsheet format under a separate file name that is referenced in the metadata field of the main data base.

2) Similar summary tables will 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), will be evaluated by comparing them against the QA/QC warning and control limit criteria for accuracy, precision, and blank contamination specified in Table 5-3.

4) Method detection limits reported by the laboratory for each analyte will be tabulated and compared against the target values in Table 5-1.

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 QA/QC report containing the narrative explanation of any QA/QC deviations will 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 BPTCP program.

5.5.3.3 Assigning Data Codes and Data QA/QC Qualifier Codes

Data Codes

As previously indicated, BPTCP chemistry laboratories are expected to assign only two data codes ("-8" and "-9") to data fields. These are not data QA/QC qualifier codes, and will only be used in the actual analyte data fields, not in data QA/QC qualifier code fields. Other laboratories also have specific data codes that will be utilized in their specific data fields (such as toxicity). For chemistry laboratory data reports, the data code "-8" denotes that the sample was analyzed for a particular analyte but the specific analyte was not detected; the data code "-9" denotes that the sample was not analyzed for a particular analyte or group of

analytes, for whatever reason (i.e., the analysis was not authorized by the SWRCB, the sample was contaminated and unable to be analyzed, the container broke, etc.).

Data QA/QC Qualifier Codes

Data QA/QC qualifier codes are notations used by laboratories and data reviewers to briefly describe, or qualify, data and the systems producing data. QA/QC data qualifier codes will be entered in the Data QA field for each particular analysis performed by the chemistry laboratories prior to submission of the data to DFG. QA/QC data qualifier codes to be used by BPTCP chemistry laboratories include "-4", "-5", and "-6" only, at this time. Because some degree of expert judgement and subjectivity typically is necessary to evaluate chemistry QA/QC results and assign QA/QC data qualifier codes, data validation will be conducted only by qualified personnel. 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.

When the chemistry data meets or exceeds QA/QC requirements, the chemistry labs will assign a "-4". When the chemistry data contains minor deviations from QA/QC criteria, but is acceptably explained, data in these instances will be assigned a "-5". It is the philosophy of the BPTCP program that data which are qualified as estimates because of minor exceedance of a control limit in a QA/QC sample (the "-5" QA/QC data qualifier code) are still usable for most assessment and reporting purposes; however, the QA report should be evaluated before assessments are made for some applications that are especially sensitive or critical. When the chemistry data contains major deviations from the QA/QC criteria (major exceedances of control criteria), and cannot be acceptably explained, data in these instances will be assigned a "-6" in the QA/QC data qualifier code field. The "-6" code implies that the data is not usable for most assessments and reporting purposes.

5.5.3.4 Taking Final Action

Upon completion of the above steps, a report summarizing the QA review of the data package will be prepared, samples will be properly stored or disposed of, and laboratory data and accompanying explanatory narratives will 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 will summarize all conclusions concerning data acceptability and will 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, at a minimum, will be addressed in the QA report which is submitted to DFG (for more specific reporting requirements and report outline, see Section 11):

- 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)**

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 and toxicity testing. For the BPTCP, only the percent fines (silt+clay) will be determined for most particle size samples using the wet sieve method (DFG, 1992), while some samples will be further analyzed using a dry sieve analysis for the coarse fraction and a hydrometer analysis for the fine fraction, yielding an overall frequency histogram of all size fractions, including silts, clays, and colloidals. The techniques used are a modification of those described in Folk (1974).

6.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING TIME

BPTCP protocols for collecting particle size samples are described in detail in the DFG QAQC manual. Samples will be from aliquots of the homogenate supplied to all laboratories. A minimum sample size of 100 grams is recommended. Samples will be held and shipped on ice (NOT dry ice) and may be stored at 4°C for up to one year before analysis.

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 will be conducted even if samples were homogenized in the field.

Furthermore, all screens used for dry sieving 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 analytical balance, drying oven, sieve shaker, dispersant solution concentration, and temperature bath used in the analysis will be calibrated at least monthly. Dried samples will be cooled in a desiccator and held there until they are weighed. If a desiccator 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 desiccator will be checked periodically, and, if necessary, the ground glass rims will be greased or the "O" rings will be replaced.

While wet sieve analysis is a robust and reliable method of measuring percent fines with few inherent problems other than those of sieve cleaning and sample recovery mentioned above, hydrometer analysis is a more involved process and is subject to certain potential sources of inaccuracy. These include actual concentration and amount of dispersant present in the hydrometer cylinders, calibration of hydrometers, and temperature effects on density and particle settling rates. Dispersant concentrations and amounts used for the analysis will be carefully measured and standardized for all samples. The hydrometers used for the analysis are pre-calibrated in a reference cylinder using the techniques of Lewis (1984). If during the course of the analysis, the water temperature changes by greater than 2°C, then the hydrometer corrections are re-measured by re-calibrating each hydrometer in a reference cylinder. Thorough mixing of the silt-clay suspension at the beginning of the analysis is also critical. A perforated plexiglas disc plunger is very effective for this purpose. Once the analysis begins, the hydrometer 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 taking hydrometer readings.

Quality control for the sediment analysis procedures will be accomplished primarily by performing replicate analyses on a randomly selected subset of samples from each batch. A batch is defined as one group of samples from a given leg or sampling event. Approximately 10% of each batch of samples will be aliquoted into two subsamples after thorough homogenization and the subsamples will be analyzed with the appropriate technique (wet sieve or dry sieve/hydrometer analysis). If the coefficient of variation (CV) of the fractional percentage for any particle size class is greater than 10% for any sample analyzed in replicate, all samples from that batch must be re-analyzed. In addition, the laboratory protocol and/or technician's practices will be reviewed and corrected to bring the measurement error under control. If the CV of all particle size fractions is less than 10% for all replicate samples, the mean of the two values obtained will be reported and the sediment analysis process will be considered in control.

6.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

6.4.1 Sample Tracking

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 BPTCP project coordinator. Laboratory personnel will be aware of the required sample holding times and conditions for particle size samples, and there will 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 will be reported to the nearest 0.01 gram dry weight. The laboratory will report the results for all samples analyzed (including QC duplicates) both in hard copy and in a computer-readable format specified by the BPTCP Project Coordinator.

In addition, both the paper and electronic data packages will 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. The report submitted to the BPTCP coordinator shall include the following:

- A cover letter, both on paper and in electronic file format, providing a brief description of the procedures and instrumentation used 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 concentrations of the analytes of interest (reported in units identified to three significant figures unless otherwise justified). Concentration units will be % (dry weight). All data will be double entered to check for accuracy and the report signed by the laboratory manager or designee. The data shall conform to the approved BPTCP Data Base Description.

- 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. The data will be submitted to the data processing manager in dBase 4 format. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted.

The Project Coordinator will 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 BPTCP'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 the Project coordinator to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. The Project Coordinator

will monitor and formally document each step in the data evaluation process as it is completed. This documentation will be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist will 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 will 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. In the BPTCP, this will include the following specific steps:

- Project personnel will 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) will be parsed and entered into the BPTCP project database to verify that the correct format has been supplied.

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

The Project Coordinator will 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 will 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, will begin after project personnel have determined that the data package is complete. Data validation for particle size data will 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 will be calculated. For any station having an RSD greater than 20%, all raw data and calculations will 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. 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 will be prepared, samples will be properly stored or disposed of, and laboratory data will be archived both in a storage file and in the database. Reports documenting the results of the QA review of the data package will summarize all conclusions concerning data acceptability and will 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 will 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.

SECTION 7

MARINE TOXICITY TESTING

7.1 OVERVIEW

The process for relying on toxicity assessment to identify Toxic Hot Spots is described briefly in the Introduction of this document. A more thorough discussion follows. First, existing data (State Mussel Watch, sediment chemistry, and toxicity) are reviewed for the likely presence and absence of toxicity. Screening of these sites (and others selected at random or likely to be degraded and nondegraded) follows and consists of application of a battery of toxicity tests (bedded sediment, pore water, and overlying water) on single replicates. Because determination of hot spot status using toxicity testing requires recurrent toxicity associated with chemical contamination, sediment chemistry analysis is also performed during screening. Once initial data review and screening are completed, a survey is performed to ensure that adequate numbers of nontoxic (reference) sites are available for each TOC/grain size stratum. Once sufficient numbers and types of reference sites are identified, confirmation sampling is performed on groups of reference and potential toxic hot spots (sediment chemistry is repeated and three field replicates are sampled). Subsequent statistical analysis is applied to these data to determine whether distinctions exist between reference sites and suspect hot spots and whether these distinctions are associated with chemical contamination within strata. The remainder of this section presents QA/QC protocols and requirements for toxicity testing, from sample collection and laboratory analysis to validation of the resultant data.

7.2 PROJECT DESCRIPTION

7.2.1 Objective and Scope Statement

Toxicity is assessed using a number of standardized solid-phase sediment, pore water, and subsurface water toxicity tests. The Marine Pollution Studies Laboratory (MPSL) at Granite Canyon is conducting water and sediment toxicity tests using species specified by the Project Manager; candidate species are listed below. The test organisms are exposed to water or sediment samples in the laboratory, and any resulting detrimental effects are quantified, giving a numerical estimate of the sample toxicity.

7.2.2 Data Usage

Laboratory toxicity estimates give an indication of the potential threat to aquatic organisms posed by the contaminated water or sediments. Correlation of toxicity data with matching chemical data from split samples allows identification and measurement of contaminants that may be harmful to aquatic life. Potential hot spots identified by this project will be further investigated to determine the areal extent of contamination and to guide remediation efforts.

7.2.3 Technical Approach

Sediment toxicity testing at MPSL will follow standardized procedures for each organism, as specified in accepted published protocols.

7.2.3.1 Solid Phase Toxicity Tests

Solid phase toxicity tests will be conducted by placing test organisms in contact with whole sediments in test chambers filled with clean dilution water. Candidate test species and protocols for solid phase toxicity tests include:

Amphipods: *Rhepoxinius abronius* (ASTM, 1993)
Eohaustorius estuarius (ASTM, 1993)
Hyalella azteca (Nebecker et al., 1984)
Ampelisca abdita (ASTM, 1993)

Polychaetes: *Neanthes arenaceodentata* (Johns et al., 1990)

7.2.3.2 Interstitial (Pore) Water Toxicity Tests

Interstitial waters contain the water soluble fractions of sediment contaminants, and are generally considered to be the primary route of exposure for aquatic organisms in contaminated sediments (although ingestion may be the primary route for some species). Interstitial water is extracted in small volumes by squeezing or centrifuging whole sediment. Toxicity tests on interstitial water use sediment or water column organisms with protocols modified for small test solution volumes. A number of test protocols using water column organisms have been identified for use in regulating discharges to marine water portions of bays and estuaries. These protocols are listed in the State Water Quality Control Plans for Enclosed Bays and Estuaries of California and are indicated with an asterisk* in the following lists. The following is a list of organisms that have either been used previously in interstitial water tests or are easily adaptable to small test solution volumes ($\leq$ 10 ml) for interstitial water testing. The citations refer to the protocols to be used at MPSL.

Bivalve larvae	**Crassostrea gigas* (ASTM, 1993)
	**Mytilus edulis* (ASTM, 1993)
Abalone larvae	**Haliotis rufescens* (Anderson et al., 1990)
Echinoderm fertilization	**Strongylocentrotus* spp. (Dinnel et al. 1987, with modifications by EPA, 1992)
Giant Kelp	**Macrocystis pyrifera* (Anderson et al, 1990)
Red Alga	**Champia* (Weber et al., 1988)
Fish Embryos	*Atherinops* (Anderson et al., 1990)
	**Menidia* (Middaugh et al.,1988)
	Pimephales (Spehar et al., 1982)

Cladocerans *Daphnia* (Nebecker et al., 1984)

Cereodaphnia (Horning and Weber, 1985)

7.2.3.3 Ambient Water Toxicity Tests

Monitoring of toxic hot spots in the BPTCP includes evaluation of ambient water column toxicity. A number of test protocols using water column organisms have been identified for use in regulating discharges to marine water portions of bays and estuaries. These protocols are listed in the State Water Quality Control Plans for Enclosed Bays and Estuaries of California and are indicated with an asterisk* in the following list. The following are the organisms (and protocols) to be used at MPSL to test for ambient water column toxicity.

Bivalve larvae *Crassostrea gigas* (ASTM, 1993)

Mytilus edulis (ASTM, 1993)

Abalone larvae *Haliotis rufescens* (Anderson et al., 1990)

Echinoderm fertilization *Strongylocentrotus* spp. (Dinnel et al. 1987, with modifications by EPA, 1992)

Giant Kelp *Macrocystis pyrifera* (Anderson et al, 1991)

Red Alga *Champia* (Weber et al., 1988)

Mysid *Holmesimysis* (Hunt et al., 1992)

Fish Embryos *Atherinops* (Anderson et al., 1990)

**Menidia* (Middaugh et al.,1988)

Pimephales (Spehar et al., 1982)

Fish Larvae	*Atherinops* (Anderson et al., 1990)
	Menidia (Weber et al., 1988)
	Pimephales (Weber et al., 1988)
Cladocerans	*Daphnia* (Nebecker et al., 1984)
	Ceriodaphnia (Horning and Weber, 1985)

7.2.3.4 Analysis of Ammonia and Hydrogen Sulfide

Ammonia and hydrogen sulfide are two common compounds that occur naturally in sediments, although their concentrations can be increased by anthropogenic inputs. Both compounds can be toxic in the low to sub-part-per-million range, depending on test organism sensitivity. Both parameters are measured during toxicity testing to determine the concentrations to which test organisms are exposed. These are not necessarily the concentrations occurring in the field, but they are measured during toxicity testing to indicate whether test results are influenced by the presence of these compounds.

Ammonia concentrations are measured as total ammonia using the ammonia-selective electrode method (APHA, 1985). Standards are prepared at concentrations of 0.1, 1, and 10 ppm from a 1000 $\pm$ 5 ppm ammonia as nitrogen standard solution (Orion Instruments). Total ammonia measurements are recorded to two significant figures based on the standard error of replicate measurements. Unionized ammonia concentrations are calculated from total ammonia and simultaneous pH measurements, using an equation based on the partitioning coefficient of Khoo, et al. (1977). Unionized ammonia concentrations are reported to three significant figures.

Total sulfide is measured colorimetrically using the methylene blue method described by Fonselius (1985). Standards are prepared from a super stock consisting of 12 grams sodium

sulfide in one liter of deoxygenated seawater. All stock solutions and standards are prepared using seawater purged with nitrogen gas to eliminate oxygen, and stocks, standards, and samples are kept in containers flushed with nitrogen gas and maintained with a nitrogen head space. A secondary stock of approximately 4 ppm sulfide is prepared by dilution of the super stock. The sulfide concentration of this secondary stock solution is verified by iodimetric titration (APHA, 1985). Standards are prepared by individual dilution of the secondary stock at concentrations of 0.01, 0.1, 0.5, 1.0, and 2.0 ppm. Reagents are then added to the standards to develop color, which is then analyzed at 680 nm on a spectrophotometer. The resulting calibration curve is used to convert sample absorbance to concentration of total sulfide. Total sulfide measurements are recorded to three significant figures based on the standard error of replicate measurements. Hydrogen sulfide concentrations are calculated from total sulfide and simultaneous pH measurements, using an equation based on the partitioning coefficient of Savenko (1977). Hydrogen sulfide concentrations are reported to four significant figures.

Ammonia and sulfide are currently measured in the water overlying test sediments, as specified in standard testing protocols. Because overlying water is continuously aerated, these concentrations may be significantly less than those to which the burrowing test organisms are exposed interstitially. We are currently developing methods for measuring interstitial ammonia and sulfide concentrations in test containers.

7.2.4 Monitoring Parameters and Collection Frequency

The parameters to be measured, their frequency of measurement, references and other information are given in Table 1.

Table 7-1. Monitoring Parameters

Parameter	Sampling Frequency	Test Replicate Sampled	Immediate Processing or Measurement	Reference
Rhepoxinius				
Survival	Termination	All Chambers	Sieve & record	ASTM, 1993
Eohaustorius				
Survival	Termination	All Chambers	Sieve & record	ASTM, 1993
Ampelisca				
Survival	Termination	All Chambers	Sieve & record	ASTM, 1993
Hyalella				
Survival	Termination	All Chambers	Sieve & record	ASTM, 1993
Neanthes				
Survival	Termination	All Chambers	Sieve & record	Johns et al., 1990
Initial Ind. Wt.	Initiation	3 groups of 5	Sieve & record	
Final Total Wt.	Termination	All Chambers	Sieve & record and divide by # to get mean individual wt.	
Bivalve larvae				
Normal shell development	Termination	All chambers	Fix larvae in formalin, examine w/microscope, record initial loading density & final number of live normal larvae	ASTM, 1993
Haliotis				
Normal shell development	Termination	All chambers	Fix larvae in formalin, examine w/microscope, record # normal & abnormal	Anderson, 1990
Echinoderm Fertilization				
Presence of Fertilization Membrane	Termination	All Chambers	Fix eggs/embryos in formalin, examine microscopically, record number fertilized and unfertilized	Dinnel et al.1987 modified as in EPA, 1992
Macrocystis				
Germination	Termination	All Chambers	Examine microscopically and record	Anderson, 1990
Growth	Termination	All Chambers	Measure with ocular micrometer	
Champia				
Cystocarp production	Termination	All Chambers	Examine microscopically and record	Weber et al 1988
Holmesimysis				
Survival	Daily	All Chambers	Count and remove dead	Hunt et al., 1992
Growth	Termination	All Chambers	Examine microscopically and measure length	

Table 7-1. Monitoring Parameters (Continued)

Parameter	Sampling Frequency	Test Replicate Sampled	Immediate Processing or Measurement	Reference
Atherinops				
Survival	Daily	All chambers	Record number survive, remove dead.	Anderson, 1990
Dry weight	After 7 day	All chambers	Dry surviving larvae, weigh, record to nearest 0.1 mg	
Menidia beryllina				
Survival	Daily	All chambers	Record number survive, remove dead.	Weber et al 1988
Dry weight	After 7 day	All chambers	Dry surviving larvae, weigh, record to nearest 0.1 mg	
Pimephales				
Survival	Daily	All chambers	Record number survive, remove dead.	Weber et al 1988
Dry weight	After 7 day	All chambers	Dry surviving larvae, weigh, record to nearest 0.1 mg	
Daphnia				
Adult Survival	Daily	All Chambers	Record number survive, remove dead.	Nebecker, 1984
Number of live young	Daily	All Chambers	Record and remove.	
Total live young	Termination	All Chambers	Sum and Record	
Most young by any one adult	Termination	All Chambers	Sum and Record	
Cereodaphnia				
Adult Survival	Daily	All Chambers	Record number survive, remove dead.	Mount and Norberg, 1984;
Number of live young	Daily	All Chambers	Record and remove.	Horning and Weber, 1985
Total live young	Termination	All Chambers	Sum and Record	
Most young by any one adult	Termination	All Chambers	Sum and Record	
All Tests				
Reference Toxicant	Beginning and end of test	Stock solution and highest concentration	Pour into clean 30 ml polyeth. vial, acid. w/1% Q-dist. HNO_3	Anderson et al., 1990; Bruland et al., 1979

Table 7-1. Monitoring Parameters (Continued)

Parameter	Sampling Frequency	Test Replicate Sampled	Immediate Processing or Measurement	Reference
Total ammonia (unionized NH_3 can be calculated based on pH)	Test start & end	Overlying water in test chamber	Record to 2 sig. digits within calibration curve range of 0.01 to 100 ppm	APHA, 1985 Sec. 417E Khoo et al 1977
Dissolved oxygen	0, 48, 96, and 144 h	Overlying water, pore water; one rep/sample	Record to nearest 0.01 mg/L	APHA, 1985 Sec. 421F
pH	0, 48, 96, and 144 h	One replicate of each sample	Record to nearest 0.01 pH unit	APHA, 1985 Sec. 423
Salinity	0, 48, 96, and 144 h	One replicate of each sample	Record to nearest 1 ‰	Anderson et al., 1990
Temperature	Continuous	In temp control room	Record to nearest 0.5°C	Anderson et al., 1990
	Daily	In six test containers	Record to nearest 0.5°C	Anderson et al., 1990
Hydrogen sulfide	Test start & end	Overlying water in test chamber	Record to 3 sig. digits within calibration curve range of 0.01 to 100 ppm	APHA, 1985 Savenko, 1977 Fonselius, 1985

7.3 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

This section describes methods used at MPSL to determine the precision, accuracy, representativeness, comparability, and completeness of data generated in toxicity studies. The primary data generated in toxicity testing is the degree of response observed in test organisms exposed to environmental samples or toxicant compounds, although secondary data such as dissolved oxygen concentration are also collected.

The degree to which toxicity test data can be used to adequately assess the effects of contaminants in the field is determined by study design, sample handling, measurement error, and appropriate statistical analysis. All field sites, regardless of contamination, vary in a number of characteristics, including sediment grain size, total organic carbon (TOC) content, oxidation state, and infaunal assemblage. In order to resolve differences due to contamination, the natural variation among uncontaminated reference sites must be determined. Samples from reference sites are tested to characterize inherent site variability, and to establish a benchmark against which to compare contaminated sites. In addition to reference samples, control samples are also tested. Tests conducted on control water or sediments serve to verify the health of the test organisms and assure the proper maintenance of test conditions such as lighting, temperature, organism handling, and cleanliness of test equipment. When amphipods are used as test organisms, control sediments (often called "home sediments") are collected at the same time and place as the test organisms. With other infaunal test organisms, control sediments are well-sorted, fine-grain sand, usually collected at the *Rhepoxynius* collection site, or collected at remote sites with a well documented history of low toxicity. In aqueous tests, controls are samples of clean laboratory dilution water. Brine controls are included whenever brine is used to adjust sample salinity. Brine controls are prepared by mixing hypersaline brine with distilled water and dilution water to reach the test salinity. Brines are made by freezing filtered natural seawater until the remaining liquid is at the appropriate salinity (approximately 70‰). Data from tests on control samples are used primarily for quality assurance purposes to determine whether the tests meet test acceptability criteria.

Outlined below are the quantitative data quality objectives (DQOs), and the equations used to calculate accuracy, precision, and completeness of the data.

7.3.1 Data Quality Objectives

7.3.1.1 Precision

Toxicity test precision can be estimated by comparing: 1) the variation among laboratory replicates of each sample, and 2) the results of multiple tests using reference toxicants. Depending on the protocol used and the goals of the study, three to five laboratory replicates are analyzed for each sample tested. There are no established criteria for acceptable levels of between-replicate variability, but standard deviations can be compared to those produced in similar studies to gauge the precision of test data.

Precision of dissolved oxygen, pH, salinity, total sulfide, and total ammonia analyses will be determined as the CV of triplicate measurements. Measurements of appropriate standard solutions will be taken at the beginning, middle, and end of each series of sample measurements, with a maximum of 20 sample measurements in between. If the CV exceeds 10% for dissolved oxygen, pH, salinity or total sulfide, or if the CV exceeds 30% for ammonia, corrective action will be taken, and analyses conducted since the previous triplicate analysis will be repeated.

Reference toxicant tests are used to verify the sensitivity of the test organisms by measuring their response to a dilution series of a toxicant for which there is sufficient previous information to establish an expected response. Since the toxicity of the reference material is assumed to be constant, the results of reference toxicant tests can be used to determine the precision of the test system, as described below. Reference toxicant tests will be performed for all tests, using water only as the test medium. (Solid phase reference toxicant tests are not conducted in this study because insufficient information is available on spiking techniques and expected responses of test organisms).

For each reference toxicant test, a point estimate is generated which indicates the reference toxicant concentration corresponding to a given level of effect. For tests using a lethal endpoint, the trimmed Spearman-Karber method is used to generate a median lethal concentration (LC_{50}) as the point estimate. For tests using a sublethal dichotomous endpoint, such as percent normal larval shell development, the trimmed Spearman-Karber method is used to generate the median effective concentration (EC_{50}) as the point estimate. For tests using a sublethal continuous endpoint, such as growth inhibition, the EPA Inhibition Concentration percentage (ICp) statistical program is used to generate the median inhibition concentration (IC_{50}) as the point estimate. Toxicity test precision (P) is given as the coefficient of variation (CV) among repetitive reference toxicant test point estimates. The CV is the standard deviation (sd) divided by the mean (X) of multiple point estimates.

$$P = CV = sd/X \times (100\%).$$

Acceptability of reference toxicant test precision has not been specified for all test protocols to be used in this project. In general, toxicity test precision of 40% or less is considered acceptable (Rue, et al., 1988). The coefficient of variation for all reference toxicant tests performed as part of this project will be reported as an estimate of test precision.

Precision of dissolved oxygen, pH, salinity, and temperature will be determined as the CV of triplicate measurements. Triplicate measurements will be taken at the beginning of each series of measurements and on a minimum of 5% of all samples measured. If the CV exceeds 5% for any of the above parameters, the analyses conducted since the previous triplicate analysis will be repeated.

7.3.1.2 Accuracy

Toxicity test accuracy cannot be determined, because there is no "true" or "correct" response against which to compare the results of a toxicity test. All organisms are inherently different in their response to contaminants, and organisms cannot be calibrated against standards. There are no data quality objectives for toxicity test accuracy.

Accuracy of water quality parameter measurements will be assessed on a regular basis at the beginning and end of each set of measurements by comparing the measured value of a standard against the known value of the standard. Accuracy will be expressed in terms of the relative error as the percent deviation of the measured value from the known value. Accuracy is calculated as follows:

$$RPD = [V_m - V_k]/V_k \times (100\%)$$

where: RPD = the relative percent difference
Vm = the measured value,
Vk = the known value.

If an RPD value exceeds 10% for dissolved oxygen, pH, salinity, or total sulfide, or if the RPD exceeds 30% for ammonia, corrective action will be taken, and analyses conducted since the previous triplicate analysis will be repeated.

7.3.1.3 Representativeness

The degree to which laboratory toxicity measurements represent actual effects of contaminated sediments to exposed organisms in the field is determined by a number of factors, including: sampling design, number and characteristics of reference sites (see above), sampling gear, sample handling, test species used, and exposure time. All of these factors have been determined for this project by personnel external to the Marine Pollution Studies Laboratory.

7.3.1.4 Comparability

Comparability of toxicity data is based on knowledge of the species used, the test conditions, and the results of concurrent reference toxicant tests. Standard species and protocols will be used in this study, and test conditions of temperature, salinity, pH, and dissolved oxygen will be controlled and monitored during the course of the toxicity tests. Reference toxicant tests (positive controls) using standard toxicants will be conducted concurrently to assess the relative sensitivity of the test organisms. Control seawater and control sediments (negative

controls) will be used to determine the "blank" response of the test organisms used. By generating and documenting the above information during this study, the toxicity of samples tested at MPSL can be compared to that of other samples elsewhere if the other samples are tested using the same standard species, protocols, and reference toxicants.

7.3.1.5 Completeness

It is anticipated that all of the samples received at our laboratory will be tested. There are a number of components that must be successfully completed in order to generate acceptable toxicity data for each sample, including: acceptable control response, acceptable reference toxicant test results, acceptable levels of variation in test conditions, and dependable supply of suitable test organisms. Since only some test species for this project are cultured at our facility (others are purchased commercially), and because of the vagaries of dealing with test organisms in the laboratory, some level of test failure is expected, estimated at 20%. For this reason, an additional sample is requested from each site to allow retesting of any samples that are not successfully tested initially. A completeness percentage of 95% is anticipated, given sufficient sediment to allow one retest of each sample if necessary. Because of constraints on sample collection, retested sediments will be older than originals. We will re-test sediments only if they have been properly stored for a period of not longer than six weeks.

7.4 SAMPLING AND LABORATORY PROCEDURES

Sampling for this project is being conducted by others (see project organization chart, Section 2). General laboratory procedures are referenced in Section 3B. Standard operating procedures are on file or under development at the Marine Pollution Studies Laboratory at Granite Canyon.

7.5 SAMPLE CUSTODY PROCEDURES

Sample labelling and custody procedures have been developed by the BPTCP sample collection team at the Moss Landing Marine Laboratories. Samples of chain of records forms are available in the Quality Assurance Project Plan for sampling.

At the Marine Pollution Studies Laboratory, the QA/QC Officer is responsible for custody of all incoming samples. The QA/QC Officer maintains the chain of records, which are photocopied and maintained in separate original and back-up copy files. The QA/QC Officer maintains the sample tracking log that follows all samples through all stages of laboratory handling and analysis. The sample tracking log includes sample identification numbers, location and condition of storage, date and time of each removal and return to storage, the signature of the person removing and returning samples, and the final disposition of samples. All custody forms and sample log entries are independently verified at the end of each test run. All sample custody information is cross checked before data is released in reports to DFG and the State Board. Original chain-of-records, sample tracking logs, data report sheets, and quality control records will be sent to DFG, if requested, when data is reported. Copies will be kept at MPSL.

7.6 CALIBRATION PROCEDURES AND PREVENTATIVE MAINTENANCE

Calibration procedures at the Marine Pollution Studies Laboratory are necessary for five types of equipment used in the project. There are no preventative maintenance schedules for any analytical equipment used in the project.

7.6.1 Calibration

Dissolved oxygen, pH, and ammonia are measured using an Orion EA 940 expandable ion analyzer. The oxygen probe is zeroed electronically and calibrated against water-saturated air before each series of measurements, as recommended by the manufacturer. Manufacturer's stated relative accuracy for dissolved oxygen is $\pm$ 0.002 ppm, and

repeatability is ±0.002 ppm.The pH probe is calibrated against two pH buffers (7.0 and 10.0) before each series of measurements. Manufacturer's stated relative accuracy for pH is ± 0.002 pH units, and repeatability is ± 0.002 pH units. Calibration for ammonia and sulfide measurement is described in Section 7.2.3.4.

A Leica temperature compensating refractometer is used to measure test solution salinity. It is calibrated at the beginning and end of each series of measurements using a seawater sub-standard that was measured to the nearest 0.001 ‰ on a Beckman salinometer calibrated to Wormley water. Measurement on the refractometer is accurate to ± 1‰.

Temperature is measured using standard mercury thermometers that are calibrated semiannually to an ASTM certified thermometer factory calibrated to NIST standards.

Temperature control units for constant temperature rooms, water baths and incubators are checked twice daily and adjusted when necessary to maintain correct temperature.

Reference toxicant stock solutions are prepared using a Mettler AE 163 balance. The balance is self calibrating by means of adjusting a calibration weight lever during an electronic calibration procedure. This calibration procedure is performed monthly.

7.6.2 Preventative Maintenance

There are no manufacturer's recommended preventative maintenance procedures for the instruments listed above. Probes are stored in their proper storage solutions, and probe membranes are changed according to manufacturer's recommendations.

7.7 DOCUMENTATION, DATA REDUCTION AND REPORTING

7.7.1 Documentation

Raw data is recorded in non-erasable ink on standardized printed data sheets. Test solution water quality measurement data is recorded on the back of the same sheet. Original data sheets are copied twice; then the three sheets are labeled as "original", "working copy", and

"archive copy". Each is stored in a separate file cabinet. The original is submitted to the funding agency, if requested, as part of the corresponding project report. The working copy is used to enter data into computer data base and statistics programs. The archived copy is stored in the archive file. Print outs of descriptive and comparative statistics are attached to the working copies for reference when compiling data interpretations for reports.

7.7.2 Data Reduction and Reporting

Raw data from data sheets will be entered into a data base programmed by Rick Packard of Ecoanalysis, the contractors responsible for data management on this project. Data will be entered by two people using a double entry program that automatically checks for errors in transcription.

Each site will be characterized by descriptive statistics indicating the mean response and variation among replicates for each sample. Statistically significant differences among sites will be determined by analysis of variance (ANOVA). Individual comparisons can be made using multiple range tests, such as the Student-Neuman-Keuls test for identifying groups of sites based on toxicity, or the Dunnett's test for comparing sites within gradients or against a control. These data analysis strategies will be based on the use of field replicates to determine the variance for estimating statistical significance. In some cases, where strict confirmation of toxicity results is not required, sites may be sampled without field replication. ANOVA techniques may be used in such cases only with the caveat that using laboratory replication underestimates the variance associated with field collected samples. In addition, some variability exists between sites regardless of the presence of toxicity. Use of multiple reference sites allows characterization of between site variation in the absence of toxicants. Further review of experimental designs by qualified statisticians is recommended to reconcile the logistical difficulties of sampling multiple reference sites with the formal data requirements for adequate analysis.

Data will be provided in a format that allows correlation with physical and chemical data gathered at other laboratories. This will allow analysis of correlation between toxicity and

contaminant concentration, particle size, or other parameters. Data will be reported graphically where needed for data interpretation.

Reference toxicant data will be reported as means and standard deviations for each reference toxicant treatment, accompanied by the no observed effect concentration (NOEC), the median lethal, effective, or inhibition concentration (LC_{50}, EC_{50}, or IC_{50}), and the mean control response. Original data sheets will be included for all reported results.

7.8 DATA VALIDATION

All data for this project will be checked immediately following initial analysis for any obvious outliers, transcription errors, or excessive variations among laboratory replicates. Any suspect counts will be re analyzed under the microscope to verify correct sample analysis. Results of negative controls will then be checked to verify that they meet test criteria. Sample data will then be validated by double data entry into the laboratory data base. Data tables will be reviewed at each subsequent step of data manipulation to assure that no changes occur during transfer to the DFG data base or transfer to statistical programs for analysis. Additionally, the UCSC Toxicity Project QC Officer will review all sample logs and data forms to ensure that requirements for sample holding times, sample preservation, sample integrity, data quality assessments, and equipment calibration have been met. At the discretion of the Project Officer, data which do not meet these requirements will either not be reported or will be reported with an explanation of associated problems.

In addition, reference toxicant tests (using water only exposures) will be conducted concurrently to all sediment tests using organisms from the same lot or shipment to determine the suitability of the organisms and test conditions. Reference toxicant test results will be compiled into control charts and cumulative coefficients of variation to provide a continuous assessment of test organism condition and toxicant sensitivity throughout the course of the project. Responses of test organisms to negative controls, both clean (home) sediment and clean (laboratory) dilution sea water will be reported to verify compliance with

test acceptability criteria. Data from sediment tests will be considered valid only if the negative controls (home sediment or dilution water) meet test acceptability criteria. Variations from other test acceptability criteria will be reported, and, in cases where variations are deemed significant by the project officer in consultation with the program manager, the test will be repeated.

7.8.1 Assigning Data Codes and Data QA/QC Qualifier Codes

Data Codes

As previously indicated, BPTCP chemistry laboratories are expected to assign only two data codes ("-8" and "-9") to data fields; these same codes are also utilized by the toxicity laboratory, with one additional data code assigned to be used in toxicity data fields: "-7". These are not data QA/QC qualifier codes, and will only be used in the actual analyte data fields, not in data QA/QC qualifier code fields. Other laboratories also have specific data codes that will be utilized in their specific data fields. For toxicity laboratory data reports, the data code "-8" denotes that the a sample was analyzed for a either ammonia or hydrogen sulfide in the overlying water of toxicity test containers, but the specific compound (ammonia or hydrogen sulfide) was not detected; the data code "-9" denotes that the sample was not analyzed for a particular bioassay, for whatever reason (i.e., the analysis was not authorized by the SWRCB, the sample was contaminated and unable to be analyzed, the container broke, etc.); the data code "-7" denotes that the sample was authorized to be analyzed for the urchin mitotic aberration bioassay (urchin cytogenetics), and the test was conducted, but because of the particular endpoint for this test, the data is entered as "unreadable" ("-7") if the endpoint is unable to be distinguished. This code ("-7") is also used in some instances where statistical analyses were not performed for reasons explained in the QA report.

Data QA/QC Qualifier Codes

Data QA/QC qualifier codes are notations used by laboratories and data reviewers to briefly describe, or qualify, data and the systems producing data. QA/QC data qualifier codes will be entered in the Data QA field for each particular bioassay or analysis performed by the toxicity laboratory prior to submission of the data to DFG. QA/QC data qualifier codes to be used by the BPTCP toxicity laboratories include "-3", "-4", "-5", and "-6" only, at this

time. Because some degree of expert judgement and subjectivity typically is necessary to evaluate toxicity QA/QC results and assign QA/QC data qualifier codes, data validation will be conducted only by qualified personnel. 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.

When the toxicity data meets or exceeds QA/QC control criteria requirements, the toxicity lab will assign a "-4". When the toxicity data contains minor technical violations of QA/QC test control criteria, but the violation is acceptably explained and is unlikely to affect assessment of test results, data in these instances will be assigned a "-3", and is considered valid by toxicity testing project officer. When the toxicity data contains minor non-technical deviations from QA/QC test control criteria, and the data is usable for most purposes and is acceptably explained, but may possibly affect test results, data in these instances will be assigned a "-5". It is the philosophy of the BPTCP program that data which are qualified as estimates because of minor exceedance of a control limit in a QA/QC sample (the "-5" QA/QC data qualifier code) are still usable for most assessment and reporting purposes; however, the QA report should be evaluated before assessments are made for some applications that are especially sensitive or critical. These data (coded "-5") should be discussed with the toxicity project testing officer before using. When the toxicity data contains major deviations from the QA/QC test control criteria (major exceedances of control criteria), and cannot be acceptably explained, data in these instances will be assigned a "-6" in the QA/QC data qualifier code field. The "-6" code implies that the data is not usable for most assessments and reporting purposes.

7.9 PERFORMANCE AND SYSTEM AUDITS

7.9.1 Internal Audits

A log is kept of every test conducted at the Marine Pollution Studies Laboratory with corresponding information about the result and disposition of samples and data. At bimonthly intervals, the QC officer conducts an audit of sample storage areas and data files to determine whether these are in agreement with sample and data logs and records. The QC

officer will also conduct frequent checks of data sheets, calibration sheets, and accuracy and precision data sheets to make sure that persons conducting tests and taking measurements are doing so correctly.

7.9.2 External Audits

MPSL agrees to comply with and assist in any performance or system audits conducted by the DFG or SWRCB as part of this project. These audits will take place on the time schedule determined by the DFG or SWRCB, and we anticipate an external audit at or near the time of project initiation by the SWRCB QA officer.

7.10 CORRECTIVE ACTION

Data quality objectives and validation procedures for this program have been designed to ensure that personnel will be able to quickly identify and correct analytical problems. Should the results of data validation measures indicate that the integrity of data associated with the sample set is questionable, the analyses would be repeated. Quality assurance audits of the program have been proposed in the work plan to ensure that work is performed by individuals who understand the objectives and methods to be used. Audit results will be documented and reported to the Project Officer who will be responsible for implementing all necessary corrective actions.

7.11 REPORTS

Data reports shall be submitted as specified in Authorization/Instructions to Process Samples forms as issued by the DFG Project Coordinator and accepted by the Marine Pollution Studies Laboratory UCSC Toxicity Testing Project Officer. Data reports will include all data generated under the specific authorization, any requested descriptive and comparative statistics resulting from data analysis, a written description of any deviations from standard testing procedures, and a checklist detailing QA criteria and the degree to which each is met or compromised. Reports shall be submitted in both hard copy and electronic formats as specified in Instruction/Authorization forms. Other reporting requirements will be as agreed upon by the program management and the UCSC Toxicity Testing Project Officer.

SECTION 8

MACROBENTHIC COMMUNITY ASSESSMENT

8.1 OVERVIEW

Benthic assessment to identify Toxic Hot Spots proceeds in much the same fashion as toxicity assessment. Existing data (State Mussel Watch, sediment chemistry, toxicity, and benthic composition) are reviewed for the likely presence and absence of benthic degradation. Screening of these sites (and others selected at random or likely to be degraded and nondegraded) follows and consists of observations collected by diving or otherwise viewing the site (e.g., boat-based sediment collection). In contrast to toxicity assessment, benthic determination of hot spot status does not require repeat demonstration of degradation. Once initial data review and screening are completed, a survey is performed to ensure that adequate numbers of nondegraded (reference) sites are available for each stratum (e.g., grain size, TOC, dissolved oxygen, etc.). The full set of field measurements (see section 3.4.3) is taken at these sites to supplement this process. Once sufficient numbers and types of reference sites are identified, confirmation sampling is performed on groups of reference and suspect hot spots, field measurements are taken, field replicates are included, and sediment chemistry is performed. Subsequent statistical analysis is applied to these data to determine whether distinctions exist between reference sites and suspect hot spots and whether these distinctions are associated with chemical contamination within strata.

This section presents BPTCP 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. Sampling is conducted from mid summer to early fall each year prior to the development of major winter storm events. Five (5) replicate benthic samples are obtained at each site from five (5) separate deployments of the sampler. Each sample is processed individually in the laboratory to obtain an accurate assessment of species diversity, abundance, and biomass.

8.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING TIME

This is explained in detail in Section 3. In summary, 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 this document. In particular, field personnel will be thoroughly trained in the proper techniques for sieving and sample preservation (using a 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 will not be extruded from the upper face of the sampler such that organisms may be lost
- Overlying water will be present (indicates minimal leakage)
- The sediment surface should be relatively flat (indicates minimal disturbance or winnowing)
- The entire surface of the sample will 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 will be rejected.

In the laboratory, catalogued and stored samples must be easily retrieved and protected from environmental extremes. Samples cannot be allowed to freeze and will be stored above 5 °C to prevent the formation of paraformaldehyde. Temperatures greater than 30 °C will be avoided so as to retard evaporative losses. Stored and archived samples will be checked periodically, but not less than every six months, for excessive evaporative losses due to loosely-fitting or cracked container lids, or inadequately sealed jars.

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 in the following sections.

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. (Note: Occasionally, BPTCP benthic analyses include checking 100% of residues or resorts). These resorts will 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. Experienced sorters or taxonomists will 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. Sorters are required to sign and date a Milestone Progress Checksheet for each replicate sample processed.

The results of sample resorts may require that certain actions be taken for specific technicians. 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 specimens are discovered within sample residues, they will be removed by the Benthic QA Officer and placed in the appropriate vial. 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 will never be re-checked by the technician who originally processed the sample.

Ideally, each batch of ten samples processed by an individual taxonomic technician will be from a similar habitat type (*e.g.*, all oligohaline stations) or the same taxonomic group (e.g., polychaetes). The recheck of one out of the ten samples in a batch will be done periodically and in a timely manner so that subsequent processing steps and data entry may proceed. As each taxon is identified and counted during the recheck, the results will be compared to the original data sheet. Discrepancies will be double-checked to be sure of correct final results. Following re-identification, specimens will be returned to the original vials, labelled with project, date collected, site and or station information, and IDORG.

All changes in species identification will be recorded on the original data sheet (along with the date and the initials of the person making the change) and these changes will be entered into the database. However, the numerical count for each taxonomic group will not be corrected unless the overall accuracy for the sample is below 90%. The results of all QC rechecks of species identification and enumeration will be recorded in a timely manner in a separate logbook maintained for this purpose.

Taxonomic identifications will 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 will be established. This collection will consist of representative specimens of each species identified in samples from Southern and Northern California. For some species, it may be appropriate to include in the voucher specimen

collection individuals sampled from different geographic locations within the State. The verified specimens will 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 will 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 project coordinator 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 will 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 will be made of waterproof, 100-percent (at least) rag paper, pre-printed labels identifying the project, date collected, site/station information, and idorg. A separate label will identify the enclosed specimen(s) with the current nomenclature. 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 will 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 parafilm wrapped in a clockwise direction. The species (and other taxonomic designation) will be written clearly on the outside and on an internal label. Reference specimens will 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 will be maintained by the laboratory performing the identifications.

Reference collections are invaluable, and will be retained at the location where the identifications were performed. In no instance will this collection be destroyed. A single person will be identified as curator of the reference collection and will 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

Biomass measurements will be determined using either wet weight or by volumetric estimates. 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. 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

BPTCP information management personnel have developed a comprehensive system for cataloguing and archiving sample containers. 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. 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 will be recorded directly onto standardized data forms. 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 will be designed so that all necessary information is recorded clearly and unambiguously; data will be recorded in ink and signed by the responsible person. Completed data sheets and QA/QC forms will be kept in bound notebooks arranged by type; these forms will be made available to the Project Coordinator upon request and will be inspected for adequacy during QA audits. The following information will be provided to the Project Coordinator:

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

- Tabulated results in hard copy form including a field for sample identification that corresponds to the sample IDORG as described in the DFG BPTCP database description. All data will be double entered to check for accuracy and the report will be signed by the laboratory manager or designee. The data shall conform to the approved DFG BPTCP Data Base Description.

- 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. The data will be submitted to the data processing manager in dBase 4 format, converted from Microsoft Exel. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted.

- Results for all QA/QC samples 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 batch number is described in the Data Base Description and is a field in the dBase database. Each type of analysis (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analysis, TOC and grain size, and AVS) will have it's own unique batch number. In addition, to the batch number field, another field will be included in all data sets (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analysis, TOC and grain size, and AVS) that lists the file names that contain the QA data for that sample. This field is also described in the database. The laboratory will denote QA/QC samples using the codes (abbreviations) and reporting units specified in Table 5-6. This field is described in the database and will be entered into each of the data sets by each of the laboratories.

Laboratory managers will 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 includes, for example, data entry procedures that involve double entry of information from the laboratory data sheets 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 QC Officer will perform manual checks on a random subset of all transcribed data sheets (at least 10% of the total) to verify transcription accuracy.

The laboratory will report the results for all samples both in hard copy and in a computer-readable format specified by the Project Coordinator. At a minimum, the following information will be included: BPTCP sample ID, laboratory sample ID (if applicable), numbers of individuals per sample for each species (i.e, abundance), and number of species per taxonomic grouping (i.e. polychaetes, crustaceans, molluscs, echinoderms, others). Tables summarizing the results of QC checks (e.g., resorts, recounts, and reidentifications) 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 DFG BPTCP Project Coordinator 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 BPTCP'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 the Project Coordinator to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. It is the responsibility of the Project Coordinator to monitor closely and formally document each step in the data evaluation process as it is completed. This documentation will be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist will 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 will 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, BPTCP personnel will 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) will be parsed into the BPTCP database to verify that the correct format has been supplied. The Project Coordinator will 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 will 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, will begin after laboratory personnel have determined that the data package is complete. Data validation for the benthic community assessment will 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 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.

8.4.4 Data Quality Reports

All QA/QC data associated with the laboratory processing of benthic samples will be presented in BPTCP 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 will be prepared, samples will be properly stored or disposed of, and laboratory data and associated commentary will be archived both in a storage file and in the database. Reports documenting the results of the review of the data package will summarize all conclusions concerning data acceptability and will 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 will 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, and changes made in sampling design, if appropriate.
- 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.

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 BPTCP 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 based upon criteria developed by the USA EMAP program. 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 environmental and biological variables.

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 *apriori* 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 regions. SJSUF Principal investigators, with the oversight of the DFG BPTCP Project Manager, 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 regions in the statistical methods employed. As part of the required series of checks prescribed above, there should be an independent 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 DFG BPTCP Project Manager 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

TOTAL ORGANIC CARBON ANALYSIS

9.1 OVERVIEW

Total organic carbon (TOC) content is used to characterize the physical and biological characteristics of sediments, and can be used to normalize chemical concentrations according to sediment characteristics and to account for some of the variability found in biological assemblages and toxicity testing. For the BPTCP, the percent TOC will be determined for sediment samples using a Control Equipment Corporation Model 240-XA Elemental Analyzer.

9.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING TIME

BPTCP protocols for collecting sediment TOC samples are described in detail in the DFG QA/QC manual. Samples will be from aliquots of the homogenate supplied to all laboratories. A minimum sample size of 100 grams is recommended. Samples will be held and shipped on ice (NOT dry ice) and may be stored frozen (-18°C) for up to one year before analysis.

9.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

Quality control of sediment TOC 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 will be conducted even if samples were homogenized in the field. Any inorganic carbon (shell fragments, etc.) present in the sample will be removed by digestion with excess 1N HCl, after which samples will be repeatedly rinsed with deionized water and centrifuged until all overlying water is approximately neutral pH (6 or 7). Samples are then dried at less than

55°C and homogenized by grinding in a ball mill before analysis. All spatulas, containers, and reagents used in the analysis will be thoroughly cleaned and organic carbon-free to avoid sample contamination.

The analytical balance and drying oven used in the analysis will be calibrated at least monthly. Dried samples will be cooled in a desiccator and held there until they are weighed. If a desiccator 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 desiccator will be checked periodically, and, if necessary, the ground glass rims will be greased or the "O" rings will be replaced.

Aside from potential problems caused by storage and sample aliquoting practices, inorganic carbon artifacts, weighing errors, and sample contamination, the only other source of inaccuracy present in TOC analysis involves the calibration and performance of the elemental analyzer itself. For the purpose of minimizing and controlling errors associated with the instrument, a strict protocol of sample and standard loading will be followed. The use of standards having known organic carbon, nitrogen and hydrogen concentrations allows calibration of the instrument and interpretation of the results. Samples are run in sets of 64, including blanks and standards. The elemental analyzer is conditioned and equilibrated prior to the running of each new batch by combusting a series of 8 blanks and 6 standards. Acetanilide and BCSS-1 standards will be run at intervals of every 5 samples to insure the reliability of TOC readings. Forceps and spatulas used in the weighing procedure are flamed every 20 samples to eliminate contamination and variance in sample material weights. Sediments and standards are analyzed as 1 to 5 mg subsamples weighed to the nearest 1 ug into organic carbon-free aluminum combustion sleeves.

Quality control for the sediment TOC analysis procedures will be accomplished both by performing replicate analyses on a randomly selected subset of samples from each batch and by evaluation of results from standards. A batch is defined as one group of samples from a

given leg or sampling event. Accuracy of analyses will be determined using the relative percent error (RPE) of individual and mean TOC measurements of standards having a known concentration of carbon. If the RPE of a TOC measurement for any standard exceeds 10%, all measurements conducted since the previous (passed) accuracy check will be repeated. Furthermore, approximately 10% of each batch of sediment samples will be aliquoted into two subsamples after thorough homogenization and the subsamples will be analyzed separately. If the coefficient of variation (CV) of the percent organic carbon is greater than 10% for any sample analyzed in replicate or for the standards analyzed, all samples from that batch must be re-analyzed. In addition, the laboratory protocol and/or technician's practices will be reviewed and corrected to bring the measurement error under control. If the CV of the percent organic carbon is less than 10% for all replicate samples, the mean of the two values obtained will be reported and the sediment TOC analysis process will be considered in control.

9.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

9.4.1 Sample Tracking

The laboratory responsible for processing the sediment TOC 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 BPTCP project coordinator. Laboratory personnel will be aware of the required sample holding times and conditions for TOC samples, and there will be clearly-defined custody procedures for sample handling, storage, and disbursement in the laboratory.

9.4.2 Data Reporting Requirements and Evaluation Procedures

The weight of each sediment fraction will be reported to the nearest 0.01 gram dry weight. The laboratory will report the results for all samples analyzed (including QC duplicates) both in hard copy and in a computer-readable format specified by the BPTCP Project Coordinator. In addition, both the paper and electronic data packages will 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. The report submitted to the BPTCP coordinator shall include the following:

- A cover letter, both on paper and in electronic file format, providing a brief description of the procedures and instrumentation used 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 concentrations of the analytes of interest (reported in units identified to three significant figures unless otherwise justified). Concentration units will be % (dry weight). All data will be double entered to check for accuracy and the report signed by the laboratory manager or designee. The data shall conform to the approved BPTCP Data Base Description.

- 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. The data will be submitted to the data processing manager in dBase 4 format. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted.

The Project Coordinator will 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 BPTCP'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 the Project coordinator to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. The Project Coordinator will monitor and formally document each step in the data evaluation process as it is completed. This documentation will be in the form of a data evaluation tracking form or

checklist that is filled in as each step is completed. This checklist will 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 will 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. In the BPTCP, this will include the following specific steps:

- Project personnel will 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) will be parsed and entered into the BPTCP project database to verify that the correct format has been supplied.

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

The Project Coordinator will 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 will 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, will begin after project personnel have determined that the data package is complete. Data validation for particle size data will 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 TOC analysis 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 TOC samples obtained at each station will be calculated. For any station having an RSD greater than 20%, all raw data and calculations will be checked by the laboratory to ascertain that the difference truly reflects natural spatial variability among the three grab samples and not measurement error.

9.4.3 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. 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 will be prepared, samples will be properly stored or disposed of, and laboratory data will be archived both in a storage file and in the database. Reports documenting the results of the QA review of the data package will summarize all conclusions concerning data acceptability and will 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 will 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.

SECTION 10

INFORMATION MANAGEMENT

10.1 SYSTEM DESCRIPTION

The Information Management System (IMS) developed for the Bay Protection and Toxic Cleanup Program (BPTCP) is designed to perform the following functions:

- o document sampling activities and standard methods,
- o document sample tracking and shipments,
- o process and organize both field, laboratory, and QAQC data,
- o perform range checks on selected numerical data,
- o facilitate the dissemination of information, and
- o archive the data.

10.2 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 BPTCP IMS will provide a foundation for the management and quality assurance of all data collected and reported during the life of the project.

10.2.1 Standardization

A systematic numbering system will be developed for unique identification of individual samples, sampling events, stations, analytical Batch numbers, 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. This unique numbering system is described in the DFG BPTCP Database Description.

10.2.2 Preprinted Labels for Sample Containers

Sample containers will be labeled with waterproof printed labels to eliminate potential confusion in the field and thereby reduce the number of incorrect or poorly-affixed labels. Containers with all the required preprinted labels, and sample sheets will be prepared from the sampling database that is created for the field crews prior to each sampling event (an event is defined as a single visit by a crew to a sampling site).

10.2.3 Data Entry, Transcription, Data Change and Transfer

In addition to paper data sheets, all data collected by field crews are recorded in a series of electronic forms after returning to the laboratory. Following the initial entry of data into the 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 authority to make changes.

A cruise report is prepared within one week of returning to the laboratory. The cruise report documents the purpose of the cruise, task order authorizing field work, and field activities such as a log of daily activities, personnel involved, problems encountered, sites sampled, latitude and longitude of station locations, etc. The BPTCP Program Coordinator for DFG reviews the data after each cruise and suspicious data is flagged for further investigation. If a change to the data is required, the data librarian is required to complete a Data Revision/Correction Form (electronic file and hard copy form) indicating the data sheet, variable, and reason for change. This information is written to a dBase-4 file. The original database containing the raw data or QAQC data will have a data correction/revision field as

described in the DFG Database Description. When satisfied that the data is 100% correct, the Data Librarian assigns an acceptance code.

10.2.4 Automated Data Verification

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 Project Coordinator, the Project Quality Assurance Officer, or their designee. This type of report will be generated routinely and will 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 Project Coordinator will review the report and release data which have passed the QA check for addition to the database. All identified errors must be corrected before flagged files can be added to a database, and as detailed above, a Data Revision/Correction Form must be completed if it is necessary to correct data. If it is found that the data check ranges are not reasonable, the values will be changed by a written request which includes a justification for the change.

Database entries which are in the form of codes will 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 will be flagged in a written report for appropriate corrective action (*e.g.*, update of the look-up table or removal of the erroneous code).

10.2.5 Sample Tracking and Instructions for Analyses

All samples will be hand delivered to the recipient laboratory by the BPTCP staff at MLML. Exceptions will have to be granted in writing by the Project Coordinator. If the samples are shipped the tracking of sample shipments from the MLML site to the analytical laboratories is extremely important in order to minimize loss of samples by the field crews, shipping carrier, receiving laboratory, or as a result of improper packaging. Shipment tracking is performed by the transfer of shipment and receipt information via daily telephone calls from

the MLML staff and receiving labs, and by the recording of shipping and receiving documents from the carrier such as UPS and Federal Express. All shipments will have the proper chain of record (COR) forms enclosed. The chain of record information is computerized and is stored in hardcopy notebook by the BPTCP Field Crew at MLML in order to ease in the tracking of a particular sample. An electronic file (diskette) containing information regarding samples being transferred will also be delivered with the hard copy coc form to the respective laboratories receiving samples for analyses. This diskette is to be returned upon delivery of products and shall contain data in dBASE-4 database format as required by DFG.

Also included with chain-of-records forms will be a checklist of analyses to be performed and expected delivery date of products, as well as any other details or instructions necessary to perform appropriate analyses. This checklist/COR package will also include the cruise report and accompanying station location maps for the sampling leg or event from which the samples originated. The checklist will also be signed and returned with the coc forms, verifying that the recipient laboratory understands and agrees to perform the analyses as outlined.

10.2.6 Reporting

Following analysis of the samples, the summary data packages transmitted from the laboratories will include results, QA/QC information, and accompanying text in a manner outlined in the coc/checklist package as detailed by CDFG. All data reports, as well as any other official BPTCP deliverable product will be submitted directly to DFG BPTCP personnel, and not to any other agency or project cooperators/funders. DFG is then responsible for timely submission of quality assured data to the SWRCB or its designees.

Any data reports not complying with all DFG data reporting criteria will be rejected and returned for correct format. All data must be submitted in previously determined dBase-4 format, and must be accompanied by an electronic file (diskette) and a hardcopy file. A Data Accuracy Verification/Data Transmittal Form shall also accompany the data report,

verifying that the data has complied with QA/QC criteria, and that it has been double-entered or double-verified according to protocol. This form will be signed by both the submitting laboratory and all appropriate DFG officials receiving/reviewing the data report and files.

If the laboratory has assigned internal identification numbers to the samples, the data report transmitted to DFG must include at a minimum the BPTCP sample identification number ("IDORG"), the CDFG Station Number, Leg Number, and any 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.

10.2.7 Redundancy (Backups)

All files in the BPTCP IMS will be backed up regularly. The main IMS data management storage system will be at MLML. A backup will be kept at Granite Canyon MPSL and updated weekly to enable the information management team to reconstruct the database in the event that one system is destroyed or incapacitated. Backups will be sent to the SWRCB and Eco-Analysis at the same time they are sent to the Granite Canyon facility. All disks and files will be numbered uniquely and registered by the BPTCP Data Librarian. Any change in data will prompt a recall of all backup disks that are registered. A Data Revision/Correction Form will be completed on every occasion which data already entered into the database is corrected or revised for any purpose. This was detailed previously.

Updates (diskettes containing the newly revised data in a database) will be sent out to the SWRCB and any other users that have registered copies of the data. At all laboratories and the BPTCP IMS center at MLML, backups will be made daily to all working files that have been changed that day. In addition, backups of all BPTCP intermediate files or correspondence files will be performed on a monthly basis and transmitted to the Data

Librarian at MLML to provide a backup in the event of a complete loss of data or files at one of the laboratories.

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 done at the SWRCB on a non-volatile medium such as an optical "WORM" disk. 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).

10.3 DOCUMENTATION AND RELEASE OF DATA

Comprehensive documentation of information relevant to users of the BPTCP IMS will be maintained and updated as necessary. Most of this documentation will be accessible by diskette. The documentation will include a database description, access control, and database directories (including directory structures), code tables, and continuously-updated information on field sampling events and their purpose, and data availability.

A limited number of personnel will be authorized to make changes to the BPTCP database. All changes will be carefully documented via the use of a BPTCP Data Revision/Correction Form (both electronic and hard-copy forms), and controlled by the Data Librarian at MLML. On-line databases which are accessible to outside authorized users will be available in "read only" form at the SWRCB at some time in the future. Access to data by unauthorized users will be limited through the use of standard security procedures. Information on access rights to all BPTCP directories, files, and data bases will be provided to all potential users.

The release of data from the BPTCP IMS to outside agencies (agencies/personnel not participating in the BPTCP) will occur on a graduated schedule, and will be made at the sole discretion of the SWRCB. 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 BPTCP Project Manager at the SWRCB. The following four groups are defined for access to data:

I. DFG BPTCP group, including the information management team, the research team, the field coordinator, the Project Manager, the Project Coordinator, the Project QA Officer and the field crew chiefs.

II. SWRCB BPTCP group-including the Project Manager, Project staff and QA officer.

III. RWQCB BPTCP users

IV. Ecoanalysis group

V. General Public - University personnel, the research community, and Federal, state and municipal agencies.

Prior to release at level V (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 various laboratories to inform the DFG Project Coordinator of the appropriate number of significant figures for each measurement, and ultimately the DFG Project Coordinator's responsibility to ensure that the data submitted to DFG reflect that level of significant figures. Requests for premature release of BPTCP data will be submitted to the SWRCB through the Project Coordinator in writing. The Project Coordinator and the Quality Assurance Officer, in consultation with the Project Manager, will make a recommendation to the SWRCB regarding whether they feel the data should be released. The final authority on the release of all data is the SWRCB Project Manager and all releases must be authorized in writing. The long-term goal for the BPTCP 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 11

QUALITY ASSURANCE REPORTS TO MANAGEMENT

A quality assurance report will be prepared by the BPTCP Project 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. A separate QA report will accompany each major sampling event and will address all QA concerns relevant to the data collected during the sampling event.

Within 30 days of each audit (field or laboratory), the QA Officer will submit a report to the DFG Project Manager (an audit form will be developed by DFG for this purpose). This report will describe the results of the audit in full detail and note any deficiencies requiring management action. The QA Officer will monitor the implementation of corrective actions in response to negative findings, and will make regular reports to the Project Manager in this regard.

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

The BPTCP Program QA Officer, with assistance from the Project Coordinator, will prepare a Quality Assurance Annual Report (QAAR). The QAAR summarizes the quality assurance activities conducted during the previous fiscal year, and describes activities planned for the upcoming fiscal year.

SECTION 12

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APPENDIX 1: Working Definition of a Toxic Hot Spot

The following draft definition provides the BPTCP with a specific working definition and a mechanism for identifying and distinguishing between "known" and "potential" toxic hot spots.

1. Known Toxic Hot Spot

A site meeting any one or more of the following conditions is considered to be a "known" toxic hot spot:

1. The site exceeds water or sediment quality objectives for toxic pollutants that are contained in appropriate water quality control plans.

   This finding requires chemical measurement of water or sediment, or measurement of toxicity using tests and objectives stipulated in water quality control plans. Determination of a toxic hot spot using this finding should rely on recurrent measures over time (at least two separate sampling dates). Suitable time intervals between measurements must be determined.

2. The water or sediment exhibits toxicity associated with toxic pollutants, based on toxicity tests acceptable to the BPTCP.

   To determine whether toxicity exists, recurrent measurements (at least two separate sampling dates) should demonstrate an effect. Appropriate reference and control measures must be included in the toxicity testing. The methods acceptable to and used by the BPTCP may include some toxicity test protocols

not referenced in water quality control plans (Table 8 in Chapter III). Toxic pollutants should be present in the media at concentrations sufficient to cause or contribute to toxic responses in order to satisfy this condition.

3. The tissue toxic pollutant levels of organisms collected from the site exceed levels established by the Office of Environmental Health Hazard Assessment (OEHHA), California Department of Health Services (DHS), United States Food and Drug Administration (FDA) for the protection of human health, or the National Academy of Sciences (NAS) for the protection of human health or wildlife. When health warning against the consumption of edible organisms has been issued by OEHHA or DHS, on a site, the site is automatically classified a "known" toxic hot spot.

   Acceptable tissue concentrations are measured either as muscle tissue (preferred) or whole body residues. Residues in liver tissue alone are not considered a suitable measure for known toxic hot spot designation. Animals can either be deployed (if a resident species) or collected from resident populations. Recurrent measurements are required. Residue levels established for the protection of human health can be applied to any consumable species.

   Shellfish: Except for existing information, each sampling episode should include a minimum of three replicates. The value of interest is the average value of the three replicates. Each replicate should be comprised of at least 15 individuals. For existing State Mussel Watch information related to organic pollutants, a single composite sample (20-100 individuals), may be used instead of the replicate measures. When recurrent measurements exceed one of the levels referred to above, the site is considered a known toxic hot spot.

3. Toxic pollutant levels in the tissue of resident or test species are elevated, but do not meet criteria for determination of the site as a known toxic hot spot, tissue toxic pollutant levels exceed maximum tissue residue levels (MTRLs) derived from water quality objectives contained in appropriate water quality control plans, or a health warning has been issued for the site by a local public health agency.

4. The level of pollutant at a site exceeds Clean Water Act Section 304(a) criterion, or sediment quality guidelines or EPA sediment toxicity criteria for toxic pollutants.

In summary, sites are designated as "known" hot spots after generating information which satisfies any one of the five conditions constituting the working definition. To use the working definition, a list of toxicity tests for BPTCP toxicity testing is provided in Table 8 (Chapter III). This list identifies toxicity tests for monitoring and surveillance activities described in regional monitoring plans and partially satisfies the Water Code requirement [Section 13392.5(a)(2)] for standardized analytical methods (Department of Fish and Game, 1993).

2. Potential Toxic Hot Spot

In addition to the identification of "known" toxic hot spots, the statute requires the identification of suspected or "potential" toxic hot spots (Water Code Section 13392.5). Sites with existing information indicating possible impairment, but without sufficient information to be classified as a "known" toxic hot spot are classified as "potential" hot spots. Four conditions sufficient to identify a "potential" toxic hot spot are defined below. If any one of the following conditions is satisfied, a site can be designated a "potential" toxic hot spot:

1. Concentrations of toxic pollutants are elevated above background levels, but insufficient data are available on the impacts associated with such pollutant levels to determine the existence of a known toxic hot spot;

2. Water or sediments which exhibit toxicity in screening tests or tests other than those specified by the BPTCP;

Abnormal Development: Abnormal development can be determined using measures of physical or behavioral disorders or aberrations. Evidence that the disorder can be caused by toxic pollutants, in whole or in part, must be available.

Histopathology: Abnormalities representing distinct adverse effects, such as carcinomas or tissue necrosis, must be evident. Evidence that toxic pollutants are capable of causing or contributing to the disease condition must also be available.

Biomarkers: Direct measures of physiological disruption or biochemical measures representing adverse effects, such as significant DNA strand breakage or perturbation of hormonal balance, must be evident. Biochemical measures of exposure to pollutants, such as induction of stress enzymes, are not by themselves suitable for determination of "known" toxic hot spots. Evidence that a toxic pollutant causes or contributes to the adverse effect are needed.

5. Significant degradation in biological populations and/or communities associated with the presence of elevated levels of toxic pollutants.

This condition requires that diminished numbers of species or changes in the number of individuals of a single species (when compared to a reference site) are associated with concentrations of toxic pollutants. The analysis should rely on measurements from multiple stations. Care should be taken to ensure that at least one site is not degraded so that a suitable comparison can be made.

Fin-fish: A minimum of three replicates is necessary. The number of individuals needed will depend on the size and availability of the animals collected; although a minimum of five animals per replicate is recommended. The value of interest is the average of the three replicates. Animals of similar age and reproductive stage should be used.

4. Impairment is associated with toxic pollutants found in resident individuals.

Impairment means reduction in growth, reduction in reproductive capacity, abnormal development, histopathological abnormalities, or identification of adverse effects using biomarkers. Each of these measures must be made in comparison to a reference condition where the endpoint is measured in the same species and tissue is collected from an unpolluted reference site.

Growth Measures: Reductions in growth can be addressed using suitable bioassays acceptable to the BPTCP or through measurements of field populations (please refer to Table 8).

Reproductive Measures: Reproductive measures must clearly indicate reductions in viability of eggs or offspring, or reductions in fecundity. Suitable measures include: pollutant concentrations in tissue, sediment, or water which have been demonstrated in laboratory tests to cause reproductive impairment, or significant differences in viability or development of eggs between reference and test sites.