APPENDIX A

EXAMPLES OF SEDIMENT QUALITY SAMPLING DESIGNS USING THE DATA QUALITY OBJECTIVES (DQO) PROCESS

The Data Quality Objectives (DQO) process is a logical progression of steps that define the question to be answered and identifies qualitatively and quantitatively the procedures and decisions necessary to address the question posed. USEPA (2000a) discusses a 7-step DQO process that leads one through each of the decision points to help ensure a successful study or program outcome.

Sediment quality monitoring studies, whether for regulatory or non-regulatory purposes, would benefit from following USEPA's DQO process in order to:

- reduce the likelihood of collecting improper or inappropriate samples
- increase the likelihood of collecting representative samples for the question asked
- decrease the chances of introduced measurement artifacts or interference due to sampling or sample processing techniques
- increase the likelihood that data, and decisions based on those data, will be scientifically defensible and accepted by those involved.

The following tables are hypothetical examples demonstrating how the DQO process could be used in addressing a few common purposes for collecting sediment quality data. The purpose of the study, or question needing to be answered, drives the input for all subsequent steps in the DQO process. Thus, sampling design, how samples are collected and manipulated, and the types of analyses chosen, should all stem from the overall purpose of the study. Many national and regional programs (e.g., NOAA's Status and Trends, USEPA's Dredge Materials Management Program, or Puget Sound Estuary Program) already have a particular purpose identified, thus giving rise to the particular sampling protocols they each use.

Example 1. Objective: Determine whether certain point and nonpoint sources are associated with sediment contamination in a lake, estuary, or river segment

DQO Element	Issues/Concerns/Information
1. State problem/available resources	• Certain point and nonpoint sources of concern • Enough resources for a small-moderate survey depending on number of analyses per station
2. Identify questions to be addressed	• How does sediment quality near these sources compare with other locations and with Ecotox Thresholds (USEPA, 1996)? How toxic are they?
3. Identify information/ measurements needed	• Use available data, source information, BPJ to identify contaminants of concern Measurements could include the following: • 10d whole sediment toxicity tests • Acute or chronic toxicity tests using interstitial water • Benthic macroinvertebrate analyses • Contaminant analyses (e.g., PAHs, PCBs, metals, pesticides) • Particle size, AVS (if metals a concern), TOC, % moisture, pH, ammonia measured for each sample • Water, pH, oxygen, conductivity/salinity overlying sediment at each site
4. Define spatial/temporal boundaries	• Sample during one index period • Surficial sediment (top 0 to 2 or up to 15 cm) of most interest • Concentrate sampling near suspected contaminant sources with some reference stations (locations removed from potential sources) as well
5. Define thresholds or decision rule for parameters of interest	• Ecotox Thresholds (USEPA, 1996), and/or other sediment threshold values for contaminants • Toxicity effect level: e.g., significantly lower survival than reference stations or survival $\leq$ 50%
6. Limits on decision errors	• Precision: $\leq$ 40% C.V. among field replicates for contaminants and toxicity • Test for differences between suspect and reference sites at $p = 0.05$ and power = 80% • Field blanks for contaminants < detection limit • Lab duplicates for contaminants yield $\leq$ 25% C.V. Toxicity test replicates $\leq$ 35% C.V. • Tox test controls meet EPA minimum performance requirements.
7. Optimize the design	• Choose targeted sampling design including reference stations • Sample when conditions most favorable for gear efficiency and personnel safety • Use grab sampler - Ponar, VanVeen, or Petersen (see Table E-1 for advantages and disadvantages) • Use GPS for site positioning (± 10m) • Composite several (determined by number of contaminant analyses desired) grabs at each site for a single sample • Take 3 replicate samples at 10% of the sites, selected at random • See flowchart for Selecting a Grab Sampler Based on Site-Specific Factors (Figure 3-2).

Example 2. Objective: Determine the status of sediment quality in a site (e.g., lake, estuary, or river segment)

DQO Element	Issues/Concerns/Information
1. State problem/available resources	• Sediment quality unknown or status was determined in the past and there is a need to determine how the quality may have changed. • Enough resources for a moderate survey depending on number of analyses per station.
2. Identify questions to be addressed	• How does sediment quality compare with Ecotox Thresholds (USEPA, 1996)? How toxic are sediments now as compared to historically?
3. Identify information/ measurements needed	• Use available data, source information, BPJ to identify contaminants of concern Measurements could include the following: • 10d whole sediment toxicity tests • Acute or chronic toxicity tests using interstitial water • Benthic macroinvertebrate analyses • Contaminant analyses (e.g., PAHs, PCBs, metals, pesticides) • Particle size, AVS (if metals a concern), TOC, % moisture, pH, ammonia measured for each sample • Water, pH, oxygen, conductivity/salinity overlying sediment at each site
4. Define spatial/temporal boundaries	• Sample during one season (index period) • Sample surficial as well as deeper sediments to obtain historical record. • Sample stations representative of the entire site or, if site contains different subareas of interest (e.g., areas having very different salinity zones or different geology/sediment particle size), representative samples of each subarea.
5. Define thresholds or decision rule for parameters of interest	• Ecotox Thresholds (USEPA, 1996), and/or other sediment threshold values for contaminants • Toxicity effect level: e.g., significantly lower survival than reference stations or survival $\leq$ 50%
6. Limits on decision errors	• Precision: $\leq$ 40% C.V. among field replicates for contaminants and toxicity • Test for differences between suspect and reference sites at $p = 0.05$ and power = 80% • Field blanks for contaminants < detection limit • Lab duplicates for contaminants yield $\leq$ 25% C.V. Toxicity test replicates $\leq$ 35% C.V. • Tox test controls meet EPA minimum performance requirements.
7. Optimize the design	• Choose probabilistic sampling design; use stratified random or multi-stage random design if interested in comparing quality with respect to certain habitat features or subareas of site, respectively. • Use a corer sampler to obtain vertical (historical) profiiles of sediment at each station. Collect and analyze samples of strata of interest. Use of a larger corer (e.g., box corer) will mean fewer cores needed per station (see Table E-2 for advantages and disadvantages of different corers.) • Use GPS for station positioning ($\pm$ 10 m). • Take 3 replicates for each type of analysis at 10% of the stations. • See Flowchart for Selecting Core Samplers Based on Site-Specific Factors (Figure 3-3).

Example 3. Objective: Determine the need for or locations of site remediation (e.g., superfund)

DQO Element	Issues/Concerns/Information
1. State problem/available resources	• Site known or suspected to contain contaminated sediments that pose an ecological and/or human health risk • Resources are available for a moderate-intensive survey
2. Identify questions to be addressed	• Does the site need to be remediated? Where at the site is sediment remediation warranted?
3. Identify information/ measurements needed	• Use previously collected data, if available, to identify contaminants of concern. If no information is available, a pilot survey, using a random sampling design, may be useful to identify potential contaminants of concern. • Measurements could include: – Contaminants of concern in whole sediment and/or interstitial water – 10 d whole sediment toxicity tests – Acute or chronic interstitial water toxicity tests – Benthic macroinvertebrate analyses – Particle size, AVS (if metals a concern), TOC, % moisture, pH, ammonia to help interpret chemical or toxicological data.
4. Define spatial/temporal boundaries	• Sample over one or more index periods depending on assumed or measured rates of sediment or contaminant movement. • Surficial as well as deeper sediments may need to be sampled depending on depth of contamination. • Sampling all areas of the site may be necessary to locate areas in need of remediation unless more information is available.
5. Define thresholds or decision rule for parameters of interest	• Contaminant levels exceed Ecotox Thresholds (USEPA, 1996). • Toxicity effect level: e.g., significantly lower survival than reference sediment and < 50%.
6. Limits on decision errors	• Precision: ≤ 40% C.V. among field replicates for contaminants and toxicity • Test for differences between suspect and reference sites at $p = 0.05$ and power = 80% • Field blanks for contaminants < detection limit • Lab duplicates for contaminants yield ≤ 25% C.V. Toxicity test replicates ≤ 35% C.V. • Tox test controls meet EPA minimum performance requirements.
7. Optimize the design	• Choose systematic or grid sampling design if no previous information available on areas of contamination. • Choose targeted design if information is already available on areas of contamination within the site. • Choose multi-stage design if more than one area of contamination within the site is known but locations of contamination within each area are not precisely known. • Use grab sampler if remediation will involve only surficial sediments, or sediment depth is known to be shallow (see Table E-1 and Figure 3-2). • Use corer if remediation is likely to involve deeper sediments. For areas in which remediation may entail very deep sediments (> 2 m), consider using a vibracorer or piston corer (see Table E-2 and the Flowchart for Selecting Core Samplers Based on Site-Specific Factors (Figure 3-3).

APPENDIX B

EXAMPLES OF MEASUREMENT QUALITY OBJECTIVES USED IN SEDIMENT QUALITY MONITORING STUDIES

In the Data Quality Objectives (DQO) framework (discussed in Chapter 2 and examples presented in Appendix A of this Manual), a key element of this process is defining the thresholds or decision rules (Step 5, Figure 2-2) and the limits on errors pertaining to those decisions (Step 6, Figure 2-2). Both of these steps are critical to the DQO process, and the success of a study, because they explicitly define whether a particular result qualifies as an effect of interest, and when and where something might need to be done to mitigate or address a given observed effect. Also, these steps are critical factors in designing a tiered or phased sampling program. Thresholds, for example, can be initially set to identify problem areas with high accuracy (low decision error). This would be followed by a second sampling, with a lower threshold, to identify emerging or more subtle problems in a cost-effective manner.

The information used to help derive meaningful threshold or decision rules, and the tolerable errors associated with those rules, is collectively referred to as Measurement Quality Objectives (MQOs). MQOs are qualitative or quantitative statements that describe the type of data quality needed to support or refute a given decision. These statements explicitly define acceptable precision, bias, and sensitivity required of all analyses in the study and therefore, should be consistent with the expected performance of a given analysis or test method (ITFM 1995). Thus, if a particular whole sediment toxicity test is expected to yield 80% survival among control replicates, the MQO for control survival should be $\geq$ 80% for that test. Further, if one intends to compare sediment toxicity results between a reference station and test stations, it is important to set the number of replicates and the decision rule appropriately so that the study can determine with reasonable power and confidence whether a given sediment sample is toxic to the test organisms. The number of replicates performed will depend on the expected variability of a given test endpoint and the sensitivity desired in the study.

The following summarizes four different examples of sediment quality studies or programs, each with a different study purpose, and the types of MQOs they used. These examples are for illustrative purposes and are not meant to imply that these are the only acceptable ways in which MQOs can be derived. The examples provided are:

- Shoreline ecology program following the Exxon Valdez oil spill in Alaska
- Great Lakes Assessment and Remediation of Contaminated Sediment (ARCS) Program
- An example of an EMAP study design in the St. Louis River, Minnesota/Wisconsin
- A focused assessment in Burlington Harbor, VT in Lake Champlain
- Excerpts from Washington Department of Ecology's Sampling and Analysis Plan Guidance (WDE, 1995).

This latter guidance demonstrates how a particular program addresses sampling and analysis needs depending on the monitoring objective. The guidance also provides an interesting comparison of overall sampling procedures and sampling design considerations for two programs: WDE's Sediment Management Standards Program and the Puget Sound Dredged Disposal Analysis Program, both of which have some common monitoring objectives.

Example 1: Shoreline Ecology Program for Prince William Sound, Alaska, Following the *Exxon Valdez* Oil Spill

Background

A comprehensive shoreline ecology program was designed to assess recovery in Prince William Sound following the *Exxon Valdez* oil spill on March 24, 1989 (Page et al., 1995a; b; Boehm et al., 1995; Gilfillan et al., 1995; Gillfillan et al., 1999). The spill resulted in the release of about 258,000 barrels of Alaska North Slope crude oil into the marine environment. Nearly 500 miles of shorelines in the sound were oiled to some degree.

Project Objectives

The shoreline ecology program was designed to assess the recovery of hundreds of miles of oiled shorelines in Prince William Sound by using a limited number of sampling stations. The number of sampling stations had to be small enough for a survey to be accomplished in the summer weather window, but large enough to detect important spill effects. The study design consisted of two field components: fixed sampling locations and stratified random sampling locations. The 12 fixed locations provided information on the changes in amount and composition of petroleum residues over the period 1989-1991 to assess the rate of shoreline recovery and oil loss. Stations chosen represented worst-case oiling conditions and reference sites. Data gathered from these sites were used to assess oil loss, oil weathering, and bioavailability of oil residues to mussel communities.

The stratified random sampling (SRS) of 64 sample locations permitted results to be generalized to the affected area of the sound. The SRS survey of the spill area shoreline was divided into four habitats which characterized over 99% of the shoreline of interest, and four oiling levels which produced information on all shoreline spill levels. The matrix of four habitats by four oiling levels, with each cell containing four replicates, constituted a reasonable compromise between project cost, the need to complete sampling within the short Alaskan summer, and the need for statistical power. The principal objective was to compare means within strata (habitat/oiling level) and not to obtain overall estimates (see Table B-1).

Specific natural variables, including wave exposure, percentage sand, percentage silt/clay, and total organic carbon (TOC) were also quantified, and served as covariates in statistical analyses of oil effects.

Precautions were taken to minimize the possibilities for petroleum hydrocarbon contamination of field samples by:

- positioning the ship's stern into the wind to prevent stack gases from blowing onto the sampling equipment during deployment, recovery, and subsampling
- cleaning equipment just prior to arriving on station
- ensuring that the sampling equipment was never deployed or recovered through oil slicks or sheens
- closing the top access doors to the sampler when it was not being deployed or cleaned
- field blanks were collected from each piece of equipment at regular intervals

- potential sources of hydrocarbon contaminants were also collected to enable their identification later

Sample documentation included station logs and chain-of-custody forms. All sediment samples were logged in on the chain-of-custody forms along with other important information (station, date, time, sampling equipment and method, subsampling method, and type of sample.) Any additional information was also noted. This form accompanied each sample during shipping to the analytical lab and each sample cooler was sealed with a custody seal which was initialed and dated by the packer.

Several analytical laboratories were needed to process and analyze the large numbers of samples collected. A laboratory standard oil was analyzed with each analytical batch to monitor analytical precision and to provide data for interlaboratory comparisons. Duplicate precision for both subtidal sediment studies and 1991 deep subtidal studies was ±30%. Other MQOs are listed in the Table B-1.

Table B-1. Measurement quality objectives for subtidal sediment studies in Prince William Sound oil spill study (Gilfillan et al. 1995).

Parameter	Subtidal Sediment Studies	1991 Deep Subtidal Studies
Units	µg/kg dry weight	µg/kg dry weight
Practical Quantification Limit (PQL)	10	1.0
Estimated Method Detection Limit (MDL)	1.0	0.1
Procedural Blank	5 x MDL	5 x MDL
Field Blank	5 x MDL	5 x MDL
Matrix Spike Recovery	40 - 120%[a]	40 - 120%[a]
Surrogate Recovery	40 - 120%[b]	40 - 120%[b]
Duplicate Precision	± 30%	± 30%
EVC Control Oil Standard Precision	± 20%	± 20%
Katalla Control Oil Standard Precision	NA	± 20%
NIST SRM 1941 Precision	NA	± 25%
NIST SRM 1291 Accuracy	NA	± 15%

[a] The average percentage recoveries for all 16 compounds must fall between 40 and 120%. Only one compound can be below its minimum percentage recovery. This allowed a deviation for a single analyte of not less than 10% for chrysene and benzo(a) pyrene and not less than 20% for the others.

[b] Surrogate recoveries must fall between 40 and 120%. The upper control limit may be exceeded by one compound.

[c] The average percentage difference for the target compounds should not exceed 20% of the mean of all previous values, and no single compound/isomer grouping should deviate by more than 30% of its mean value of all previous determinations.

[d] SRM = Standard reference material.

Example 2: Measurement Quality Objectives used in the Great Lakes Assessment and Remediation of Contaminated Sediment (ARCS) Program

Background

Although toxic discharges into the Great Lakes and elsewhere have been reduced in the last 20 years, persistent contaminants in sediments continue to pose a potential risk to human health and the environment (GLNPO 1994). Elevated concentrations of contaminants in bottom sediments and associated adverse effects have been found throughout the Great Lakes and connecting channels. The extent of sediment contamination and its associated adverse effects have been the subject of considerable concern and study in the Great Lakes community.

To address these concerns, Annex 14 of the Great Lakes Water Quality Agreement between the United States and Canada (as amended by the 1987 Protocol) stipulates that the cooperating parties will identify the nature and extent of sediment contamination in the Great Lakes, develop methods to assess impacts, and evaluate the technological capability of programs to remedy such contamination. The 1987 amendments to the Clean Water Act, authorized GLNPO to coordinate and conduct a 5-year study and demonstration projects relating to the appropriate treatment of toxic contaminants in bottom sediments. To fulfill the requirements of the Act, GLNPO initiated the Assessment and Remediation of Contaminated Sediments (ARCS) Program. ARCS is an integrated program for the development and testing of assessment techniques and remedial action alternatives for contaminated sediments. Information from ARCS Program activities will help address contaminated sediment concerns in the development of Remedial Action Plans (RAPs) for all 43 Great Lakes Areas of Concern (AOCs, as identified by the United States and Canadian governments), as well as similar concerns in the development of Lakewide Management Plans.

Program Objectives

Sediments are associated with impairment of beneficial uses at 42 of the 43 Great Lakes AOCs. Prior to addressing the potential need for remediation of those sediments, the following questions are addressed:

- Are the sediments sufficiently “contaminated” to warrant consideration for remediation? In this context, “contaminated” refers to the presence of chemicals in the sediments that have the potential to cause adverse effects in humans or ecological receptors.

- Is there evidence indicating that existing concentrations of sediment contaminants are adversely affecting ecological receptors? In other words, can it be shown that the presence of contaminants in the sediments is causing adverse effects in organisms, either organisms naturally occurring in the environment, or those exposed to sediments in controlled, laboratory toxicity tests?

- Are ecological receptors exposed to the sediments bioaccumulating chemical contaminants to the extent that the resultant body burdens are adversely affecting the organisms themselves or other organisms higher in the food chain, including humans?

- If the sediments are judged to be sufficiently contaminated to be causing such effects, what is the spatial extent (i.e., both horizontal and vertical) of the contamination, and what are the implications of the distribution of contaminants on possible remedial alternatives?

Early in the ARCS Program, it was recognized that the current state of sediment assessment methods was rapidly evolving. The sediment assessment methods currently available consider a wide variety of endpoints and effects, which differ in their suitability and sensitivity for investigating sediment contamination. Therefore, assessment methods selected in the ARCS Program, reflect site- and program-specific objectives of the study being conducted.

The ARCS Program developed several measurement quality objectives (MQOs) that it uses in the design and conduct of studies at AOCs. Table B-2 summarizes these MQOs.

Table B-2. Examples of the measurement quality objectives for inorganic and organic chemistry analyses of sediment used by the ARCS program in the Great Lakes (GLNPO, 1994).

Parameter	MDL[a] (µg/kg)	Accuracy[b]	Frequency	Precision[c]	Frequency [d]
Total organic carbon	0.03%	± 20 percent	1/batch[d]	≤ 20 percent	1/batch
Oil and grease	10,000	± 20 percent	1/batch	≤ 20 percent	1/batch
pH	N/A	± 0.1 unit	1/batch	± 0.1 unit	1/batch
Acid-volatile sulfides	1,000	N/A	N/A	≤ 20 percent	1/batch
Organohalogens[e]	0.03	± 20 percent	1/batch	≤ 20 percent	1/batch
Total sulfur	10,000	± 20 percent	1/batch	≤ 20 percent	1/batch
Total solids	1,000	N/A	N/A	≤ 20 percent	1/batch
Volatile solids	2,000	N/A	N/A	≤ 20 percent	1/batch
Particle size[f]	1,000	windows	1/batch	≤ 20 percent	1/batch
Solvent extractable residue	1,000	± 20 percent	1/batch	≤ 20 percent	1/batch
Moisture content	1,000	N/A	N/A	≤ 20 percent	1/batch
PAHs	200	± 20 percent	1/batch	≤ 20 percent	1/batch
Pesticides	10	± 20 percent	1/batch	≤ 20 percent	1/batch
PCB/congener	0.5	± 20 percent	1/batch	≤ 20 percent	1/batch
PCB/Aroclor®	20	± 20 percent	1/batch	≤ 20 percent	1/batch
PCDDs/PCDFs	0.002	± 20 percent	1/batch	≤ 20 percent	1/batch
Methylmercury	10	± 20 percent	1/batch	≤ 20 percent	1/batch
Tributyltin	10	± 20 percent	1/batch	≤ 20 percent	1/batch
Metals[g]	2,000	± 20 percent	1/batch	≤ 20 percent	1/batch

Table B-2 (continued). Examples of the measurement quality objectives for inorganic and organic chemistry analyses of sediment used by the ARCS program (GLNPO, 1994).

Parameter	MDL[a] (µg/kg)	Accuracy[b]	Frequency	Precision[c]	Frequency
Except:					
Arsenic	100	± 20 percent	1/batch	≤ 20 percent	1/batch
Cadmium	100	± 20 percent	1/batch	≤ 20 percent	1/batch
Mercury	100	± 20 percent	1/batch	≤ 20 percent	1/batch

Note: ARCS - Assessment and Remediation of Contaminated Sediments
MDL - method detection limit
N/A - not applicable
PAH - polynuclear aromatic hydrocarbon
PCB - polychlorinated biphenyl
PCDDs/PCDFs - polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans

[a] Units presented in the subheading are applicable to all parameters unless otherwise noted.
[b] Accuracy is determined from a certified reference material, standard reference material, or standard and is measured from the known concentration.
[c] Precision is calculated as percent relative standard deviation. Precision requirements listed here are for analytical replicates only; field duplicates are required to have a relative percent difference ≤ 30 percent.
[d] A batch is a sample group (usually 10-20 samples) that is carried through the analytical scheme simultaneously.
[e] The MDL for chlorine and bromine is 30 ng, while the MDL for iodine is 10 ng.
[f] A soil sample with acceptance windows per size fraction was provided for use as an accuracy standard.
[g] Metals include arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc. Exceptions are noted where different methodologies are used during the metals quantification.

Example 3: Sediment Toxicity, Contaminant Concentrations and Benthic Community Structure as Indicators of Sediment Quality in the St. Louis River: A Test of EMAP Concepts Applied to a Great Lakes Area of Concern

Background

The International Joint Commission (IJC) has designated 43 areas of concern (AOCs) throughout the Great Lakes as threatened by conventional pollutants, heavy metals, toxic organic compounds, habitat alterations, and introduction of undesirable species. Results of these disturbances have been biological impacts (e.g., benthic macroinvertebrate and fish community degradation), human health effects (fish consumption advisories), and beach closings. The geographic areas associated with the AOCs contain a majority of the population residing in the Great Lakes basin, and comprise approximately 50% of all Canadian citizens.

The St. Louis River AOC, which drains a watershed of 3,634 square miles in northern Minnesota and Wisconsin, forms a large freshwater estuary that represents the second largest tributary to Lake Superior. The 12,000-acre estuary is characterized by a diversity of habitat types. The AOC is unique among the Great Lakes AOCs in that the range of habitat types and contamination status is extreme: for example, the lower estuary contains two federal Superfund sites located across the river from large, undisturbed tracts of forested land currently providing excellent habitat quality for a large variety of species. The outer harbor contains actively dredged shipping channels and a number of current or former municipal and industrial effluent discharges, as well as the world's largest freshwater sand bar, which is home to numerous endangered or threatened plants and animals.

This project has a two-fold purpose: (1) determine if the EMAP intensified grid provides a sampling framework that can be used, with structural modification, to assess AOCs; and (2) develop a set of generic environmental indicators based on biological and chemical measures for long-term assessment of AOCs using the EMAP-Great Lakes and Surface Water EMAP indicators.

In order to achieve these stated purposes, the project has four goals:

1. To test the application of the Great Lakes-EMAP design features in the Harbors and Embayments resource class.

2. To identify percentage areas within the St. Louis River AOC having acceptable and subnominal quality with respect to sediment contamination, toxicity and benthic community structure, and to associate statistically certain sediment contaminants with observed ecological effects.

3. To serve as a baseline status-and-trends monitoring survey of the St. Louis River ecosystem health.

4. To determine the sampling intensity required to survey a complex Great Lakes AOC in order to apply this knowledge to other AOCs within Region V.

The project will sample 120 sites within three habitat classes in the St. Louis River AOC for sediment toxicity, chemical contaminant concentrations, and benthic community structure. The three habitat classes are: (1) ship channels and areas in the lower estuary greater than 18 ft in depth, (2) areas of the estuary less than 18 ft in depth, and (3) Thomson, Forbay and Fond du Lac reservoirs in the lower St. Louis River.

The distribution of sampling points in the three habitat classes is as follows: 30 sites in ship channels and deep water areas, 30 sites in the reservoirs, and 60 sites in the shallow-water estuarine areas. Sampling locations were selected based on the Great Lakes-EMAP grid for habitat classes 1 and 2, and a 7^5-fold enhancement for habitat class 3. These numbers were determined through consultation with EMAP statisticians at ERL-Corvallis. Each site will be sampled twice during the two-year project period in order to estimate the short-term temporal variability for all three assessment metrics. Split-sample, surface sediments will be used for toxicity, chemistry and benthic assessment.

Project Objectives

The questions to be answered by and/or objectives for this project are the following:

1. What percentage of the sediments in the St. Louis River AOC have unacceptable levels of sediment contamination, toxicity, and benthic community disturbance?

2. Make statistical associations on an AOC-wide basis between contaminant levels and sediment toxicity or sub-nominal benthic community status.

3. How many sampling sites and time points are necessary to characterize sediment quality, using the criteria determined in Objective 1, in each of the identified habitat classes (i.e., ship channels and deep holes, shallow shoal or stream areas, and upstream reservoirs)?

4. Establish a relevant integrity index for benthic community assessment for the St. Louis River using the EMAP sampling design.

The requirements for precision, accuracy, completeness, representativeness and comparability of the data in order to attain the project objectives are described in Table B-3. Objective #1 has the least strict data quality requirements for toxicity and chemistry because the large number of samples was designed to provide an excessively-thorough site characterization. This was done in order to increase the likelihood of obtaining a wide variety of sediment types with which to carry out Objectives #2 and #3. In other words, the number of sites and sampling points is most likely overly abundant to address Objective 1. However, because this project is intended as a pilot to actually establish the requisite number of samples on an areal basis for each habitat type, an overestimate was required in the sample design. Thus, fewer sites should be required to answer Objective #1 than to satisfy Objectives 2 and 3; therefore, the required data attributes for Objective #1 are slightly less strict than for the other objectives. Objective #4 does not require data for toxicity and chemistry.

Table B-3. Summary of measurement quality objectives for the St. Louis River area of concern sediment quality assessment by sampling goal

Objective-Metric	Precision	Accuracy	Completeness	Representativeness
Goal 1	40% RPD[a]	N/A	80%	80%
#1-Toxicity	40% RPD[a]	N/A	80%	80%
Benthos	30% RPD	N/A	80%	80%
Chemistry	50% RPD	50-125%	90%	90%
Goal 2	30% RPD	N/A	90%	90%
#2-Toxicity	30% RPD	N/A	90%	90%
Benthos	30% RPD	N/A	90%	90%
Chemistry	40% RPD	70-125%	90%	90%
Goal 3	30% RPD	N/A	90%	90%
#3-Toxicity	30% RPD	N/A	90%	90%
Benthos	30% RPD	N/A	90%	90%
Chemistry	40% RPD	70-120%	90%	90%
Goal 4	N/A	N/A	N/A	N/A
#4-Toxicity	N/A	N/A	N/A	N/A
Benthos	30%	N/A	90%	90%
Chemistry	N/A	N/A	N/A	N/A

[a] Relative percent difference

Example 4: Ecological Effects of Sediment-Associated Contaminants in Inner Burlington Harbor, Lake Champlain

Background

Inner Burlington Harbor of Lake Champlain has received numerous toxicants from point and nonpoint sources in its watershed. Previous sediment sampling and analyses (Watzin et al., 1997) demonstrated relatively high concentrations of silver, lead, and PAHs in the harbor, especially in the southern end, compared to sites outside the breakwater. Much of this area corresponds to an old sewage outfall and oil dolphins but could also represent migration of inputs from the old rail yard and nonpoint sources in and around Burlington. Because the surficial sediment (top 2-3 cm) at most sites had lower pollutant concentrations than sediments at greater depths, inputs of pollutants in recent history (past 30 years) may be declining. However, these studies also indicated substantial temporal and spatial heterogeneity with respect to sediment contaminant concentrations and toxicity (Watzin et al., 1997).

Biological assessments, using benthic macroinvertebrates, were used in conjunction with other field and laboratory analyses to help determine the effects of sediment contamination and other stressors on the biota of Burlington Harbor.

Project Objectives

The overall objective of this project was to assess the hazard resulting from toxic contaminants in the sediments of Inner Burlington Harbor using a sediment quality triad approach. Because certain potentially toxic contaminants are known to occur in Burlington Harbor, the objective of this project was divided into three major component questions.

- Have toxic sediments altered benthic communities of Burlington Harbor?
- Could such changes affect other ecological components of Lake Champlain?
- Do the toxic contaminants in Burlington Harbor sediments accumulate up the food chain and cause risks to higher terrestrial and aquatic trophic levels and human health?

Sampling Design

Sampling locations in the present study were identified by reanalyzing the 1993-94 data from the harbor with a spatial statistical model known as kriging (Myers, 1988) to estimate contaminant concentrations and uncertainties throughout the harbor. Kriging is a geostatistical estimation method which incorporates a model of the spatial variability of data directly. For each chemical, a variogram was calculated using USEPA's software Geo-EAS (version 1.2.1) and fitted by a non-linear least-squared procedure.

The sampling sites selected for the present study were those with the greatest uncertainty (using existing data), and the highest likelihood of contamination. Ten sites were sampled in the harbor and 10 replicate samples from two different sites (reference sites) with relatively low contaminant concentrations and/or toxicity were sampled to help assess sediment quality in the harbor, particularly with respect to biological and toxicological measures. Five replicate samples were collected from one site inside the harbor and 5 reference samples were collected from one site. The five replicate samples collected at each reference site were tested separately for all toxicity and biological analyses, yielding five individual measures for toxicity and macroinvertebrate community structure at these two sites. Subsamples from each of the five samples collected at both sites were composited into one sample from each site for physicochemical analyses. Two other sites were

replicated once as well to obtain a measure of the variability surrounding chemical measures obtained in this study. A total of eight sites were sampled both in this study and in previous work.

Sediment Sampling and Analyses

Sites were identified using differential global positioning and checked frequently during sampling to ensure proper sampling location. Each site was sampled using five-seven petite Ponar grabs, depending on the amount of sediment collected in each grab sample. Contents of the Ponar samples from the site were composited and homogenized in the field using Teflon or high density plastic equipment to obtain a representative sample from each site for chemical, toxicological, and biological analyses.

Table B-4 summarizes the analyses performed in this study and the measurement quality objectives used. Sediment chemical analyses included PAHs, simultaneously extracted metals (SEM), total organic carbon (% TOC), acid volatile sulfides (AVS), total organic nitrogen (TON), ammonia, particle size, and pH. Five metals (those previously showing the highest levels: silver, nickel, copper, lead, and zinc) were measured. Zebra mussels (*Dreissena polymorpha*) were collected from several sites and analyzed for tissue PAHs and percent lipid content on a composite sample of organisms collected at each site. A portion of the sample from three inner harbor sites were sieved (stainless steel) to isolate the fine fraction less than 63µ and also analyzed for PAHs, total organic carbon, and organic nitrogen.

Table B-4. Summary of measurement quality objectives for precision, accuracy, and completeness of biological, toxicological, sediment, organism tissue, and field chemistry analyses conducted in Burlington Harbor (Diamond et al., 1999). RPD = relative percent difference; C.V. = coefficient of variation.

Measurement Parameter	Accuracy (% Recovery)	Precision	Completeness (%)
Benthic macroinvertebrates			
• Metric values	N/A*	• RPD≤ 20%	100
• Metric scores	N/A	• RPD≤ 5%	100
• Bioassessment scores	N/A	• RPD≤ 5%	100
Field Water Quality Measurements			85
• Conductivity	N/A	± 1% of range	
• Temperature	N/A	± 0.15° C	
• Dissolved Oxygen	N/A	± 0.2 mg/L	
• pH	N/A	± 0.2 units	
Laboratory Sediment Analyses			85
• PAH	± 25	RPD ≤ 40%	
• Ammonia	± 30	RPD ≤ 40%	
• Total organic nitrogen	± 20	RPD ≤ 40%	
• Total organic carbon	± 30	RPD ≤ 40%	
• AVS/SEM	± 30	RPD ≤ 40%	
• Particle size	N/A	RPD ≤ 20%	
Sediment Toxicity Analyses			85
• *Hyalella* 10-day acute	N/A	C.V. ≤ 30%	
• *Hyalella* 28-day chronic	N/A	C.V. ≤ 40%	
• *Pimephales* 7-day chronic	N/A	C.V. ≤ 30%	
• *Lumbriculus* 28-day bioaccumulation	N/A	C.V. ≤ 40%	
Organism Tissue Analyses			85
• PAH	± 30	RPD ≤ 40%	
• Lead	± 30	RPD ≤ 40%	
Protein Expression Analyses	N/A	RPD ≤ 20%	85

* Not applicable except through use of routine standards and calibration.

Example 5: Washington Department of Ecology Sampling and Analysis Plan Guidance

Background

The Washington Department of Ecology (WDE) provides technical guidance for developing sampling and analysis plans for sediment investigations to be conducted under the Washington Sediment Management Standards (SMS) program (WDE, 1995). Technical guidance on various aspects of sediment sampling and analysis procedures that need to be considered in the design and implementation of sediment investigations is made available through the Puget Sound Estuary Program [PSEP] protocols.

1. **Sediment Source Control Program** – Methods are described for controlling the effects of point and nonpoint source discharges through the National Pollutant Discharge Elimination System (NPDES) permit program, state water quality permit programs, issuance of administrative orders, or other mans determined appropriate by WDE; and

2. **Sediment Cleanup Program** – Administrative procedures and criteria are established to identify, screen, rank, and prioritize, and clean up contaminated surface sediment sites.

Project Objectives: Sediment Investigations Conducted under the Sediment Source Control Program

Adverse effects of contaminated sediments on biological resources and threats to human health generally will only occur when there is a pathway to ecological or human receptors. In most cases, such a pathway will only exist when surface sediments (defined by the SMS as those within the biologically active zone) are contaminated. Contaminated sediments existing at depths below the biologically active zone are unlikely to result in such effects unless the overlying sediments are removed by natural (e.g., erosion, scouring) or anthropogenic (e.g., dredging, propeller scour) means, or there are other mechanisms for the release of sediment contaminants such that exposure may occur. Additionally, the surface sediment will be most likely to exhibit impacts from recent discharges of contaminants. Hence, the focus of sediment sampling in the sediment source control process is generally on the sediments within the biologically active zone.

Table B-5 summarizes sediment management standards for biological effects criteria used by Washington Department of Ecology for Puget Sound marine sediments (WDE, 1995). These standards are, in effect, decision rules in a Data Quality Objectives context (Step 5, Figure 2-2, this Manual); cases where these standards are not met represent locations that are impaired and in need of some type of management action (e.g., remediation, follow-up sampling). WDE also has standards for many chemical contaminants (WDE, 1995) as does the Puget Sound Dredged Disposal Analysis Program (WDE, 1995).

Table B-5. Sediment Management Standards Biological Effects Criteria for Puget Sound Marine Sediments

Biological Test	Sediment Quality Standards[a]	Sediment Impact Zone Maximum Levels, Cleanup Screening Levels, or Minimum Cleanup Levels[b]
Amphipod	The test sediment has a significantly higher (t-test, $P \leq 0.05$) mean mortality than the reference sediment, and the test sediment mean mortality exceeds 25 percent on an absolute basis	The test sediment has a significantly higher (t-test, $P \leq 0.05$) mean mortality than the reference sediment, and the test sediment mean mortality is more than 30 percent greater, on an absolute basis, than the reference sediment mean mortality
Larval	The test sediment has a mean survivorship of normal larvae that is significantly less (t-test, $P \leq 0.05$) than the mean normal survivorship in the reference sediment, and the combined abnormality and mortality in the test sediment is more than 15 percent greater, on an absolute basis, than the reference sediment	The test sediment has a mean survivorship of normal larvae that is significantly less (t-test, $P \leq 0.05$) than the mean normal survivorship in the reference sediment, and the combined abnormality and mortality in the test sediment is more than 30 percent greater, on an absolute basis, than that in the reference sediment
Benthic infauna	The test sediment has less than 50 percent of the reference area sediment's mean abundance of any one of the following major taxa: Crustacea, Mollusca, or Polychaeta, and the test sediment abundance is significantly different (t-test, $P \leq 0.05$) from the reference sediment abundance	The test sediment has less than 50 percent of the reference area sediment's mean abundance of any two of the following major taxa: Crustacea, Mollusca, or Polychaeta, and the test sediment abundance is significantly different (t-test, $P \leq 0.05$) from the reference sediment abundances
Juvenile polychaete	The mean biomass of polychaetes in the test sediment is less than 70 percent of the mean biomass of the polychaetes in the reference sediment, and the test sediment biomass is significantly different (t-test, $P \leq 0.05$) from the reference sediment biomass	The mean biomass of polychaetes in the test sediment is less than 50 percent of the mean biomass of the polychaetes in the reference sediment, and the test sediment biomass is significantly different (t-test, $P \leq 0.05$) from the reference sediment biomass
Microtox®	The mean light output of the highest concentration of the test sediment is less than 80 percent of the mean light output of the reference sediment, and the two means are significantly different (t-test, $P \leq 0.05$)	Not applicable

Source: WDE (1995).

[a] The sediment quality standards are exceeded if one test fails the listed criteria [WAC 173-204-320(3)].
[b] The sediment impact zone maximum level, cleanup screening level, or minimum cleanup level is exceeded if one test fails the listed sediment impact zone maximum level, cleanup screening level, or minimum cleanup level criteria [WAC 173-204-520(3)] or if two tests fail the sediment quality standards criteria [WAC 173-204-320(3)].

WDE describes four general types of sediment monitoring (all of which are the responsibility of the discharger) that may be conducted in support of the sediment source control process:

(a) **Baseline monitoring—**Used to confirm the screening evaluation for determining potential of a discharge to cause sediment impacts conducted prior to authorization of a sediment impact zone (SIZ) to collect information that will be used in determining whether such an authorization is likely to be necessary, and to establish the baseline conditions with which future conditions can be compared

(b) **SIZ application monitoring—**Conducted to collect information to support application of the SIZ models

(c) **SIZ maintenance monitoring**—Conducted during the term of a permit that includes an authorized SIZ, with the intent to determine whether the SIZ should be renewed, reduced, or eliminated; whether areas of special importance have been adversely impacted by the discharge; and the conditions for SIZ reauthorization

(d) **SIZ closure monitoring—**Conducted following closure of an SIZ to demonstrate successful restoration of sediment quality.

The monitoring objectives vary with the type of monitoring being conducted, and the design of the monitoring program varies with both discharge- and site-specific characteristics.

Project Objectives: Sediment Investigations Conducted under the Sediment Cleanup

The Sediment Cleanup Standards set forth a decision process for identifying contaminated sediment areas and determining appropriate cleanup responses (WDE, 1995). The sediment cleanup decision process includes procedures for screening and ranking contaminated areas of sufficient concern to warrant active cleanup, as well as procedures for selecting an appropriate cleanup alternative on a site-specific basis.

Because cleanup of contaminated sediments may require their removal, sediment sampling and analyses, conducted in support of sediment cleanup studies, need to assess the total spatial extent (including both lateral and vertical) of the sediment contamination. In this respect, these sediment investigations differ from those previously described under the sediment source control process, where the focus there is generally only on sediments within the biologically active zone.

In addition to initial investigations and site characterization, which are described in by WDE (1995), there are three general types of monitoring that may be conducted in support of the sediment cleanup process:

(a) **Source control monitoring—**Conducted prior to and following sediment cleanup to determine how ongoing sources at or near a site may affect the success of active cleanup and/or natural recovery

(b) **Compliance monitoring—**Long-term monitoring conducted following cleanup actions that include containment of contaminated sediments, or to assess the progress of natural recovery and/or to evaluate recontamination of the area

(c) **Closure monitoring—**Conducted following completion of removal actions or compliance monitoring to demonstrate successful cleanup of sediment contamination. Closure monitoring must be performed before a site can be considered for delisting.

The primary objectives of sediment sampling and analyses conducted as part of a preliminary investigation of a contaminated sediment site are to: (1) Identifying sediment station clusters of potential concern, and (2) Ranking identified cleanup sites.

Such sampling and analyses must be sufficient to enable a determination of whether there are exceedances of the numerical chemical criteria or biological effects criteria (Table B-5) at three or more stations within a specific area of concern. Thus, the decision rules used by WDE in these studies (Step 5 of the DQO Process, Figure 2-2, this Manual) are defined by explicit criteria and the number of the samples demonstrating exceedence of criteria. The spatial extent of such exceedances is not required to be defined as part of a preliminary investigation (WDE, 1995).

Given the decision rules above, there are clear implications for how sampling is designed, as there need to be several samples collected and analyzed from a specific area of concern and some assurance of representative coverage of the area. At smaller sites of known or suspected sediment contamination, the addition of a relatively small number of stations or samples in a preliminary investigation is suggested by WDE (1995) to allow assessment of the spatial extent of contamination, gradients toward or away from other sources, or other important details. Hence, a single study could suffice, thereby precluding the need for a second, focused investigation.

Alternatively, if there are no plans to dredge or otherwise disturb the sediments, sampling and analyses, conducted as part of a preliminary investigation, could focus only on surface sediments. After the need for cleanup has been identified, a more focused sediment sampling and analysis program would then be required by WDE to define the spatial extent of contamination (including its vertical extent) and to evaluate cleanup alternatives.

Comparison of Data Requirements: Sediment Management Standards (Sms) and the Dredged Material Management Program (DMMP)

In addition to WDE's Sediment Management Strategy (SMS), the other major framework for sediment management activities in the Dredged Material Management Program (DMMP). The SMS and DMMP programs are very similar in the suites of biological and chemical evaluations that are required, and in the evaluation criteria that are applied. While the two programs have the same goal, protection of sediment quality, the two programs have different applications and, as a result, some differences in data requirements.

Sediment sampling and analysis is conducted under the SMS to determine whether, and to what extent, surface sediments are contaminated, whether point or nonpoint source discharges have contributed or may still be contributing to such contamination, and whether contaminated sediments should be remediated. Sediment sampling and analysis is conducted under theDMMP program to determine whether the sediment matrix (volume) proposed for dredging, when dredged and discharged at unconfined, open-water disposal sites within Puget Sound, could cause or contribute to unacceptable adverse effects on the aquatic environment. Because of these different purposes, sampling gear and compositing techniques will differ. However, both theDMMP and SMS data requirements are based upon "exposure potential" and a "sediment unit" concept. In dredging situations (DMMP), the exposure potential of concern is with the entire mass of sediments released at the DMMP sites and the sediment unit of concern is the minimum dredge unit that can be effectively managed. In SMS

situations, the exposure potential and sediment unit of concern is generally the surface, specifically the "biologically active zone" (often the top 10 cm).

DMMP sampling is designed to characterize the bulk properties of the sediments to be dredged, transported, and discharged. Sediment core samples (e.g., vibracorer) are typically collected to characterize the sediment matrix to the depth of proposed dredging for disposal determinations and to assure that the quality of newly exposed surfaces do not result in degradation. Because dredging removes the material in bulk, the cores are typically segmented on a 4-foot basis and composited across that segment (rather than further subdivided) to define a "dredged material management unit." Sediment sampling under the sediment source control process of the SMS is generally designed to characterize conditions near the sediment surface. In cases where the goal is to characterize the exposure potential, such sampling may target the biologically active zone of the sediments. In other cases, where the goal is to sample only the most recently deposited sediment, such sampling may target only the uppermost 0–2 cm of sediments. Sediment sampling designed to identify contaminated sediment sites under the sediment cleanup process of the SMS is also targeted on the near-surface, biologically active zone of the sediments. After a contaminated site is identified, however, collection of sediment cores will also generally be required to assess the vertical extent of contamination and to determine the sediment quality of any new surface to be exposed after cleanup.

The process of compositing samples from a range of depth intervals below the sediment surface may dilute higher concentrations of contaminants as pointed out in Section 2.4.3 of this Manual and in USEPA/ACOE (1998). Compositing over depth provides an assessment of the condition of the overall sediment matrix, but does not provide an assessment of the sediments within the biologically active zone. Compositing of samples from a range of depth intervals is therefore appropriate for DMMP purposes, but is ordinarily not performed for SMS investigations. In addition, many more samples may be needed for SMS purposes to establish patterns or gradients of contamination, to identify contaminant sources, or to delimit the area of contamination.

Development of Sediment Sampling and Analysis Plans

Although the specific details of individual sampling and analysis plans may be very different, all such plans submitted for review by WDE contain certain basic elements. Figure B-1 provides a recommended outline for sediment sampling and analysis plans that can also serve as a checklist for those preparing or reviewing such plans.

Each sediment sampling and analysis plan, regardless of whether it is being prepared under the sediment source control process or the sediment cleanup process, should include as part of the introduction a brief summary of site background information. The following background information should be provided:

- Site history
- Regulatory framework (e.g., NPDES; Model Toxics Control Act; SMS; Comprehensive Environmental Response, Compensation, and Liability Act)
- Summary of results of previous investigations, if any, of the site
- Location and characteristics of any current and/or historical wastewater or stormwater discharge(s) at the site

- Location and characteristics of any current and/or historical wastewater or stormwater discharge(s) in the local area

- Information on onsite waste disposal practices or chemical spills in the local area, if any

- Site location, including a location map showing the surrounding area and a site map.

The second section of a sampling and analysis plan should describe the objectives of the sediment investigation in the context of the appropriate regulatory framework (e.g., sediment source control process, sediment cleanup process). WDE (1995) provides guidance on appropriate field sampling methods; sample handling procedures; laboratory analytical methods; quality assurance and quality control requirements; data analysis, record keeping, and reporting requirements; health and safety plan; schedule; and project team and responsibilities.

Sediment Sampling and Analysis Plan Outline and Checklist

(From WDE, 1995)

1. Introduction and Background Information

- ❑ Site history
- ❑ Regulatory framework (e.g., NPDES, MTCA, SMS, CERCLA)
- ❑ Summary of previous investigations, if any, of the site
- ❑ Location and characteristics of any current and/or historical wastewater or storm water discharge(s at the site
- ❑ Location and characteristics of any current and/or historical wastewater or storm water discharge(s) in the local area
- ❑ Information on on-site waste disposal practices or chemical spills in the local area, if any
- ❑ Site location map showing the surrounding area
- ❑ Site map showing site features

2. Objectives and Design of the Sediment Investigation

- ❑ Objectives of the sediment investigation
- ❑ Overall design of the sediment investigation, including related investigations, if any
- ❑ Chemical analytes (including description of their relevance to the objectives and the regulatory framework)
- ❑ Biological tests (including description of their relevance to the objectives and the regulatory framework)
- ❑ Sampling Station Locations
  - ❑ Rationale for station locations
  - ❑ Site map(s) showing sampling stations and other pertinent features (e.g., bathymetry and current regime; outfall(s)/diffuser(s); authorized mixing zone(s), if any; sites of waste disposal, spills, or other activities that may have affected the sediments, such as sandblasting, boat repair, etc.; historical dredging activities)
  - ❑ Proposed reference stations
  - ❑ Table showing the water depth at each proposed station
  - ❑ Proposed depth(s) below the sediment surface where sediments will be collected

Figure B-1. Sediment Sampling and Analysis Plan Outline and Checklist Developed by Washington Department of Ecology (WDE, 1995).

3. Field Sampling Methods

- ❑ Station positioning methods
- ❑ Sampling equipment
- ❑ Decontamination procedures
- ❑ Sample compositing strategy and methods
- ❑ Sample containers and labels
- ❑ Field documentation procedures
- ❑ Procedures for disposal of contaminated sediments

4. Sample Handling Procedures

- ❑ Sample storage requirements (e.g., conditions, maximum holding times) for each type of sample
- ❑ Chain-of-custody procedures
- ❑ Delivery of samples to analytical laboratories

5. Laboratory Analytical Methods

- ❑ Chemical analyses and target detection limits
- ❑ Biological analyses
- ❑ Corrective actions

6. Quality Assurance and Quality Control Requirements

- ❑ QA/QC for chemical analyses
- ❑ QA/QC for biological analysis
- ❑ Data quality assurance review procedures

7. Data Analysis, Record Keeping, and Reporting Requirements

- ❑ Analysis of sediment chemistry data
- ❑ Analysis of biological test data
- ❑ Data interpretation
- ❑ Record keeping procedures
- ❑ Reporting procedures

Figure B-1 (continued). Sediment Sampling and Analysis Plan Outline and Checklist Developed by Washington Department of Ecology (WDE, 1995) (cont.).

8. Health and Safety Plan (required for cleanup investigations)

- ❑ Description of tasks
- ❑ Key personnel and responsibilities
- ❑ Chemical and physical hazards
- ❑ Safety and health risk analysis for each task
- ❑ Air monitoring plan
- ❑ Personal protective equipment
- ❑ Work zones
- ❑ Decontamination procedures
- ❑ Disposal procedures for contaminated media and equipment
- ❑ Safe work procedures
- ❑ Standard operating procedures
- ❑ Contingency plan
- ❑ Personnel training requirements
- ❑ Medical surveillance program
- ❑ Record keeping procedures

9. Schedule

- ❑ Table or figure showing key project milestones

10. Project Team and Responsibilities

- ❑ Description of sediment sampling program personnel
- ❑ Table identifying the project team members and their responsibilities

11. References

- ❑ List of references

Figure B-1 (continued). Sediment Sampling and Analysis Plan Outline and Checklist Developed by Washington Department of Ecology (WDE, 1995).

APPENDIX C

STATISTICAL CONSIDERATIONS IN DETERMINING THE APPROPRIATE NUMBER OF REPLICATE SAMPLES NEEDED AT EACH SAMPLING STATION

For certain programs or types of studies, it is desirable (or necessary) to determine if a particular location is significantly affected as compared to known non-impacted or reference locations (e.g., presence of toxicity and/or high contaminant concentrations in sediments or interstitial waters). This type of monitoring objective is used frequently in certain regulatory programs, such as the Dredged Materials Management Program and Superfund (CERCLA), however, many non-regulatory programs also have a similar objective (see for example the Burlington Harbor example in Appendix B).

If one is interested in determining statistical differences in certain measures (e.g., toxicity to *Hyalella azteca*) among or between stations, then analysis of replicate field samples may be necessary. This entails collecting multiple samples from the same station (or other spatial unit of interest), processing each sample independently, and analyzing separately each sample. For example, if the purpose of a study is to determine whether the sediment in a specific location is toxic to the estuarine amphipod *Rhepoxynius abronius* as compared to sediment from a reference location, then it is desirable to collect multiple samples from each location and perform a *Rhepoxynius* whole sediment toxicity test (including standard replication within a test) for each sample collected. Clearly, this type of replication could entail substantial laboratory effort, as compared to compositing samples from a single location and performing a single analysis or test (see Section 2.4.3 for a discussion of compositing versus replication of samples). However, compositing does not provide any information on the true variability of a given location and is rather, a form of pseudoreplication. For some programs or studies, true field replication is necessary.

The appropriate number of replicates needed for a given study depends on the statistical power and level of confidence (i.e., measurement quality objectives; see Appendix B for examples) one needs to support or refute a given decision (see Data Quality Objectives Process, Section 1.1 and Appendix A). Power is represented as $1-\beta$ and is a measure of the Type II error rate: the probability of accepting the hypothesis that the results from two different samples or stations are similar, when in fact they are not. Confidence is represented as $1-\alpha$ and is a measure of the Type I error rate: the probability of rejecting the hypothesis that the results from two different samples or stations are different when in fact they are really the same. For examples, if the question is whether a given location should be dredged for remediation purposes, the study will need to have a certain statistical power, to determine if the sediment sample from the target location is more toxic or contaminated than the reference location sediment, with a certain degree of confidence that one is making the correct decision. Both power and confidence are dependent on the expected variability in the endpoint or parameters of interest, both within a given location and within a given test or analysis. The appropriate replication, then, is required so that one has sufficient statistical power and confidence to reliably make correct decisions about the status of a given location.

To determine the number of replicates required, the following questions should be answered (Alldredge, 1987):

1. What is being compared (i.e., toxicity endpoint, parameter value)?

2. Is the significance criterion directional (is one only interested in whether a station is more toxic than another, not less toxic as well; i.e., one-tailed test)?

3. What is the level of significance between the expected and actual value of the parameter being measured?

4. How large a difference is acceptable between the expected and actual value of the criterion being measured, and with what level of probability?

5. What variability is expected in the data?

There are a number of approaches that can be used to determine the number of replicates required to achieve a minimum detectable difference at a specific confidence level and power (see Environment Canada, 1995). While many programs specify a fixed number of replicates per station (often 3-5 replicates), in other cases, this could represent too many or too few replicates for study data quality objectives. Several factors need to be defined to establish the appropriate number of replicates (see text box). U.S. EPA (2000c) presents a concise discussion of the relationships of these statistical considerations. Traditionally, acceptable coefficients of variation vary from 10 to 35%, the power from 80 to 95%, the confidence level from 80 to 99%, and the minimum detectable relative difference from 5 to 40% (Barth and Starks, 1985).

Several books on sampling design (e.g., Keith 1993; USEPA 2000b) discuss methods to determine the appropriate number of replicates needed for a given set of objectives. Table C-1 summarizes statistical approaches for determining the appropriate number of replicate samples needed per station given different study objectives.

Table C-1. Statistical Formulae for Determining Number of Samples to be Collected for Environmental Monitoring and Assessment

Study Objective	**Formula**	**Reference**
To determine the sample size required to detect an effect in an impacted area versus a control area over time:		
a) resampling same sites before and after impact and testing if the mean change in the control area is the same as that in the impacted area	$n = 2(t_\alpha + t_\beta)^2 (S/\Delta)^2$	Green, 1989
b) sampling different sites before and after impact and testing if there is no interaction between area effect and time effect	$n = 4(t_\alpha + t_\beta)^2 (S/\Delta)^2$ where: n = number of samples for each of the control and impact areas S = standard deviation Δ = magnitude of change required to be a real effect with specified power $(1-\beta)$ t_α = t statistic given a Type I[1] error probability t_β = t statistic given a Type II[2] error probability	Green, 1989

Table C-1 (continued). Statistical Formulae for Determining Number of Samples to be Collected for Environmental Monitoring and Assessment

Study Objective	Formula	Reference
To determine if the mean value for an impacted area: a) differs significantly from a standard value (e.g., sediment guideline) b) differs significantly from the mean of a control site	 $n \geq \frac{(Z_\alpha + Z_\beta)^2}{d^2} + 0.5\, Z_\alpha^2$ $n \geq \frac{(Z_\alpha + Z_\beta)^2}{d^2} + 0.25\, Z_\alpha^2$ where: n = number of samples Z_α = Z statistic for Type I error probability (e.g., α=0.05) Z_β = Z statistic for Type II error probability (e.g., β=0.90) d = magnitude of the difference to be detected (i.e., effect level)	Alldredge, 1987
To determine the number of samples required to estimate a mean value (representative of the area) with a given statistical certainty	$y\bar{x} = t_c \frac{S_x}{(n-1)^{1/2}}$ where: y = accepted error as a proportion of the mean value(e.g., y = 0.10) $\bar{x}$ = mean value of x_i (i = 1...n) S_x = standard deviation t_c = confidence coefficient (e.g., 90% or $t_{0.95}$ n = number of samples	Håkanson, 1984
To determine the number of samples required to estimate a mean	$n = \frac{(Z_{\alpha/2})^2 \sigma^2}{d^2}$ where: n = number of samples Z = Z statistic (standard normal curve) σ^2 = variance $\alpha/2$ = probability of a 95% confidence level d = distance between the center of the lower confidence and upper confidence bound	Milton *et al*., 1986

Table C-1 (continued). Statistical Formulae for Determining Number of Samples to be Collected for Environmental Monitoring and Assessment

Study Objective	Formula	Reference
To determine the number of samples required for a particular power for a normal distribution (i.e., $\bar{x} > s^2$)	$n = \frac{10^4 (t^2 s^2)}{(R^2 \bar{x}^2)} K$ where: n = number of samples t = t statistic for a desired confidence level $\bar{x}$ = mean value from preliminary sampling or historical data s = standard deviation of mean R^2 = percentage coefficient of variation K = index of clumping	Kratochvil and Taylor, 1981

[1] Type I (α) error is the probability of rejecting the hypothesis being tested when it is true.
[2] Type II (β) error is the probability of not rejecting the hypothesis being tested when it is false.

Optimizing Sampling

Having estimated the variability in a given parameter or endpoint, and the number of replicate samples per station that might be necessary to address data quality objectives, one can evaluate the cost/benefit of collecting and analyzing more or less samples in terms of the overall confidence in a given decision and the information gained. This is referred to as optimizing the study design (Step 7, Figure 2-1). Ferraro *et al*. (1994, 1989) present a method for quantitatively evaluating the optimum macrobenthic sampling protocol, including the number of replicates (*n*), which has relevance to other sediment quality studies as well. Their approach helps answer fundamental questions concerning the design of sediment quality studies such as:

- How large should the sampling unit be?
- How many replicate samples should be taken?

The procedure calculates the "power-cost efficiency" (PCE), which incorporates both the number of samples (*n*), the cost (field collection effort and lab effort combined) and the expected statistical power for each alternative sampling scheme. The various sampling schemes consist of different combinations of sampling gear, gear area, and number of replicates. The method allows determining the optimum among a set of sampling schemes for detecting differences between reference and test sites when the statistical model is a t-distribution for comparing two means. The optimum scheme can be defined as the least costly one capable of reliably (e.g., $\alpha = 0.5$, $1-\beta = 0.95$) detecting a desired difference in the means of particular measure between two sites. The approach can be applied to each parameter of interest and the results aggregated to determine the optimum protocol.

There are four primary steps in assessing the PCE of a suite of alternative sampling schemes:

1. For each scheme, collect replicate samples at paired reference and test sites. The observed difference in values between the sites is operationally assumed to be the magnitude of the difference desired to be detected. Alternatively, a percentage of the median (e.g., 20%) for a given measure calculated across reference stations could be set as the magnitude of the difference to be detected. In either case, this difference, divided by the standard deviation, is the "effect size" (ES) of interest.

2. Assess the "cost" (c_i), in time or money, of each sampling scheme *i* at each station. The cost can include labor hours for sampling, analysis, and recording results.

3. Conduct statistical power analysis to determine the minimum number of replicate samples (n_i) needed to detect the ES with an acceptable probability of Type I (α) and Type II (β) error (e.g., $\alpha = \beta = 0.05$).

4. Calculate the power-cost efficiency (PCE) for each sampling scheme by:

$$PCE_i = (n \times c)_{min} / (n_i \times c_i)$$

where $(n \times c)_{min}$ = minimum value of $(n \times c)$ among the *i* sampling schemes. The reciprocal of PCE*i* is the factor by which the optimal sampling scheme is more efficient than alternative scheme *i*. When PCE is determined for multiple metrics, the overall optimal sampling protocol may be defined as that which ranks highest in PCE for most metrics in the test set.

APPENDIX D

ADVANTAGES AND DISADVANTAGES OF DIFFERENT STATION POSITIONING TECHNIQUES

Documentation of sampling station location or position is an important aspect of field operations to ensure that: (1) sampling occurs where intended and (2) someone else (or another sampling team) could re-sample the same location at a later date. This is particularly critical for trend monitoring such as that performed by NOAA's Status and Trends Program.

With current technology, a global positioning system (GPS) device is generally the positioning method of choice because it is usually very accurate, reliable, easy to use, and affordable. However, occasionally, other positioning methods may be desired or necessary. The following tables, originally developed under the Puget Sound Estuary Program, summarize most of the positioning methods that have been used in monitoring studies, including their advantages and disadvantages.

Table D-1. Positioning methods appropriate for small water bodies (small embayment, small lakes, rivers) (modified from PSEP 1997a).

Method	Accuracy	Range	Advantages	Disadvantages
GPS or Navstar	± 100 m (0.1 to 1 m for differential GPS)	no limit on the range	• Continuous position reports available worldwide • System s available comprising a range of accuracy and cost	• Site-specific problems due to military scrambling
Theodolite	10 to 30 s ≥ ± 1 m	200 m to 5 km	• Traditional method, measuring horizontal angles between known targets • High accuracy when applied successfully • Inexpensive	• Requires triangulation between two manned shore sites or targets • Requires simultaneous measurements • Requires good visibility which limits areal coverage • Requires stationary sampling platform
Electronic Distance Measurement instrument (EDMI)	1.5 to 3.0 cm	3 km without multiple prisms	• High accuracy • Compact, portable, rugged • Relatively inexpensive • Useable for other surveying projects	• Introduces error and limitations due to reflector movement and directionality as well as ground wave reflection • Requires good line-of-sight visibility unless microwave unit is available • Requires two shore sites
Total stations	5 to 7 cm	< 5 km	• Not logistically complex, requiring single onshore site • Compatible with other uses	• Introduces limitations due to reflector movement and directionality, prism costs, and line- of- sight, optical or infrared range limitations
Sextant	± 10 s ± 3 to 5 m but variable	200 m to 5 km	• High accuracy when used nearshore by experienced operator • Portable, involving handheld device • Rapid, easy to implement • Easily obtainable • No shore party necessary • Inexpensive	• Requires simultaneous measurement of two angles • Requires good target visibility • Requires location and maintenance of targets for relocation of site • Requires calm conditions for best results • Orientation of target affects accuracy • Has limitations on acceptable angles

Table D-1 (continued). Positioning methods appropriate for small water bodies (small embayment, small lakes, rivers) (modified from PSEP 1997a).

Method	Accuracy	Range	Advantages	Disadvantages
Pelorus	variable	< 5 km	• High accuracy when used nearshore • Rapid, easy to implement • Easily obtainable • No shore party necessary • Inexpensive	• Requires simultaneous measurement of two angles • Requires good target visibility • Requires location and maintenance of targets for relocation of site • Requires calm conditions for best results • Has limitations on acceptable angles
RADAR	variable	30 to 50 km	• Standard equipment on ships • Easily operated • Yields range and relative bearing to targets	• Restricts applications by not being portable • Requires a target that reflects microwave signals
Autotape	± 0.5 m	limited	• High accuracy and precision • Portable	• High cost

Table D-2. Positioning methods appropriate for large water bodies (ocean, estuaries, large lakes) (modified from PSEP 1997a).

Category	Accuracy	Range	Advantages	Disadvantages
GPS or Navstar	± 100 m (0.1 to 1 m for differential GPS)	no limit on the range	• Continuous position reports available worldwide • System s available comprising a range of accuracy and cost	• Site-specific problems due to military scrambling
Microwave navigation systems (e.g., Miniranger, Trisponder, Racal Microfi, Del Norte)	± 1 to 3 m	25 to 80 km (depends on height of transceiver units)	• No visibility restrictions • Multiple users • High accuracy • Radio line of sight • Portable, easy system to operate	• Moderately expensive system • Requires multiple onshore sites • Cost impacts due to logistics and security of the necessary shore units • Potential source of error due to signal reflective nulls • Limited range due to low-powered shore units
Shoran	± 10 m	≤ 80 km (short range)	• High accuracy	• Limited range • Requires two shore transmitters
LORAN-C	≥ ± 15m	up to 300 km (medium range)	• No visibility or range restrictions • Requires no additional personnel • Existing equipment • Relatively inexpensive	• Incurs interference in some areas • Universal coverage not available • Used only for repositioning after employing a more geodetically precise system to identify location
Decca HIFIX/6	± 1 m	up to 300 km (medium range)	• High accuracy and precision	• Requires multiple shore sites • Expensive system
Variable range	± 0.5 °	16 to 72 km	• No visibility restrictions • Requires no additional personnel • Existing equipment • Inexpensive	• Uses line-of-sight method • Relies on map accuracies of targets • Decreased accuracy with range scale
Decca Minifix	± 2 m	≥ 70 km	• High accuracy and precision • Light weight equipment	• Expensive system
Range-azimuth	0.02 ° and 0.5 m	< 5 km (optical) 30 km (elect)	• High accuracy • Single station • Circular coverage	• User-specific • Uses line-of-sight method • Potential source of error due to signal reflective nulls • Expensive system
Satellite navigation (SATNAV)	1 - 10 m	no limit on the range	• High accuracy • Single site with minimal logistics • Use possible in restricted and congested areas • No requirement for shore sites • Capability for integrating satellite fixes with other data sources to improve precision	• Continuous coverage unavailable • Introduction of error due to local and atmospheric effects • Distorted when signal path crosses polar ice caps • Requires high initial development expenditures

APPENDIX E

ADVANTAGES, DISADVANTAGES AND ILLUSTRATIONS OF GRAB AND CORE SAMPLING DEVICES USED IN SEDIMENT MONITORING STUDIES

Table E-1. Advantages and Disadvantages of Commonly Used Grab Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995).

Device	Use	Sample Depth (cm)	Sample Volume (L^3)	Advantages	Disadvantages
Orange Peel	Marine waters, deep lakes	0 to 18	10 to 20	• Comes in a range of sizes	• Need large boat, powered winch and calbe line • Blocking of jaws may cause sample losss
Smith-McIntyre	Deep lakes, rivers and estuaries	0 to 4 (in deep sand)	10 to 20	• Reasonable quantitative samples • The trigger plates provide added leverage essential to its penetration of substrate	• Heavy, need boat and power winch • Spring loaded jaws, hazardous • Inadequate for deep burrowing organisms
Birge-Ekman, small	Lakes and marine areas; soft sediments, silt and sand	0 to 10	$\leq$ 3.4	• Handles easily without winch or crane • Can be adapted for shallow water use • Good for soft sediments, sand and silt • Allows subsampling	• Restricted to low current due to light weight and messenger activation • May exceed target penetration depth • Subsampling may be restricted by size of top flaps
Birge-Ekman, large	Lakes and marine areas; soft sediments, silt and sand	0 to 30	$\leq$ 13.3	• Can be adapted for shallow water use • Good for soft sediments, sand and silt • Allows subsampling	• Restricted to low current conditions • Penetration depth can exceed desired level due to weight of sampler • Heavy; requires winch
PONAR, standard	Deep lakes, rivers and estuaries; useful on sand, silt or clay	0 to 10	7.25	• Most universal grab sampler • Adequate on most substrates • Large sample obtained intact, permitting subsampling • Good for coarse and firm bottom sediments	• May not close completely, resulting in sample loss • Metal frame may contaminate sample • Heavy; requires winch
PONAR, petite	Deep lakes, rivers and estuaries; useful on sand, silt or clay	0 to 10	1.0	• Adequate for most substrates that are not compacted	• May not penetrate sediment to desired depth, especially in consolidated sediments. • Susceptible to incomplete closure and loss of sample. • Requires more casts to obtain sufficient sample if many analyses needed.
Van Veen	Deep lakes, rivers and estuaries; useful on sand, silt or clay; effective in marine environments in deep water and strong currents	0 to 30	18 to 75	• Adequate on most substrates that are not compacted • Large sample obtained intact, permitting subsampling • Available in stainless steel	• May not close completely, resulting in sample loss • May close prematurely in rough waters • Metal frame may contaminate sample • Heavy; requires winch
Modified Van Veen (e.g., "Ted-Young grab")	Lakes and marine areas	0 to 15	$\leq$18.0	• Fluorocarbon plastic liner can help avoid metal contamination • Screened bucket cover helps reduce bow wave effects	• Requires winch • Relatively expensive

Table E-1. Advantages and Disadvantages of Commonly Used Grab Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995).

Device	Use	Sample Depth (cm)	Sample Volume (L^3)	Advantages	Disadvantages
Petersen	Deep lakes, rivers and estuaries; useful on most substrates	0 to 30	9.45	• Provides large sample • Penetrates most substrates	• Shock wave from descent may disturb fine-grained sediment • Lacks lid cover to permit subsampling • May not close completely, resulting in sample loss • Metal frame may contaminate sample • Restricted to low current conditions • May exceed target penetration depth
Shipek, standard	Used primarily in marine waters and large inland lakes and reservoirs; not useful for compacted sandy clay or till substrates	0 to 10	3.0	• Sample bucket opens to permit subsampling • Retains fine-grained sediments effectively	• Metal frame may contaminate sample • Heavy; requires winch • Can result in the loss of the topmost 2-3 cm of very fine, unconsolidated sediment
Mini Shipek	Lakes, useful for most substrates that are soft	0 to 3	0.5	• Handles easily without winch or crane from most platforms	• Requires vertical penetration • Samples small volume • May lose fine-grained sediment • May close prematurely

Table E-2. Advantages and Disadvantages of Commonly Used Core Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995; USEPA/ACOE, 1998)

Device/ Dimensions	Use	Depth Sample (cm)	Volume Sample (L^3)	Advantages	Disadvantages
Fluorocarbon plastic or glass tube (3.5 to 7.5 cm inner diameter (I.D.); ≤ 120 cm long)	Shallow wadeable waters or deep waters if SCUBA available; soft or semi-consolidated deposits	0 to 10	0.096-0.44	• Preserves layering and permits historical study of sediment deposition • Minimal risk of contamination • Rapid; samples immediately ready for laboratory shipment	• Small sample size necessitates repetitive sampling
Hand corer with removable fluorocarbon plastic or glass liners (3.5 to 7.5 cm I.D.; ≤ 120 cm long	Same as above except more consolidated sediments can be obtained	0 to 10	0.96-0.44	• Same advantages as fluorocarbon plastic or glass tube • Penetrates substrate with greater ease through use of handles	• Small sample size necessitates repetitive sampling • Requires careful handling to prevent spillage • Requires removal of liners before repetitive sampling • Barrel and core cutter metal may contaminate sample
Box corer	Same as above but the depth of the uncon-solidated sediment must be at least 1 m	0 to 70	≤ 30.0	• Collects large, undisturbed sample; optimal for obtaining intact subsamples	• Difficult to handle • Relatively heavy; requiring larger vessel and power winch to deploy.
Gravity Corer, Phleger Corer (3.5 cm I.D., ≤ 50 cm long)	Deep lakes and rivers; semi-consolidated sediments	0 to 50	≤ 0.48	• Reduces risk of sample contamination • Maintains sediment integrity relatively well • Penetrates with sharp cutting edge	• Requires careful handling to avoid sediment spillage • Requires repetitive and time-consuming operation and removal of liners due to small sample size
Gravity Corer, Kajak-Brinkhurst Corer (5 cm I.D., ≤ 70 cm long)	Deep lakes and rivers; Soft fine-grained sediments	0 to 70	≤ 1.37	• Collects greater volume than the Phleger Corer.	• Same as Phleger Corer
Benthos Gravity Corer (6.6, 7.1 cm I.D. ≤ 3 m long)	Soft, fine-grained sediments	0 to 3 m	≤ 10.26	• Retains complete sample from tube because the core valve is fitted to the core liner • Fins promote vertical penetration	• Requires weights for deep penetration so the required lifting capacity is 750 to 1,000 kg • Requires vertical penetration • Compacts sediment sample
Alpine Gravity Corer (3.5 cm I.D.)	Soft, fine-grained, semi-consolidated substrates	≤ 2 m	≤ 1.92	• Allows different penetration depths due to interchangeable steel barrel	• Lacks stabilizing fins for vertical penetration • May penetrate non-vertically and incompletely • Requires a lifting capacity of 2,000 kg • Disturbs sediment stratas and integrity • Compacts sediment sample
Piston Corers	Ocean floor and large deep lakes; Most substrates	3 to 20 m	5 - 40	• Typically recovers a relatively undisturbed sediment core in deep waters	• Requires lifting capacity of >2,000 kg • Piston and piston positioning at penetration may fail • Disturbs surface (0 to 0.5m) layer

Table E-2. Advantages and Disadvantages of Commonly Used Core Samplers
(modified from Klemm et al., 1990; Environment Canada, 1994; PSEP, 1997a; WDE, 1995; USEPA/ACOE, 1998)

Device/ Dimensions	Use	Depth Sample (cm)	Volume Sample (L^3)	Advantages	Disadvantages
BMH-53 Piston Corer	Waters $\leq$ 2 m deep with extension rod; soft deposits	$\leq$ 2 m	$\leq$ 2	• Piston provides for greater sample retention	• Cores must be extruded onsite to other containers • Metal barrels introduce risk of metal contamination
Boomerang Corer (6.7 cm I.D.)	Ocean floor (up to 9,000 m deep)	1 m	3.52	• Requries minimal shipboard equipment so small vessels can be used	• Only penetrates 1.2 m • Requires calm water for recovery • Loses 10 to 20% of sample
Vibracorer (5.0 to 7.5 cm I.D.)	Continental shelf of oceans, large lakes; sand, silty sand, gravelly sand substrates	3 to 6 m	5.89 to 13.25	• For deep profiles it effectively samples most substrates with minimum disturbance • Can be used in over 20 m of water depth • Portable models can be operated from small vessels (e.g. 10 m long)	• Labor intensive • Assembly and disassembly might require divers • Disturbs surface (0 to 0.5 m) layer • Special generator may be needed • Heavier models require larger boat and power winch to deploy

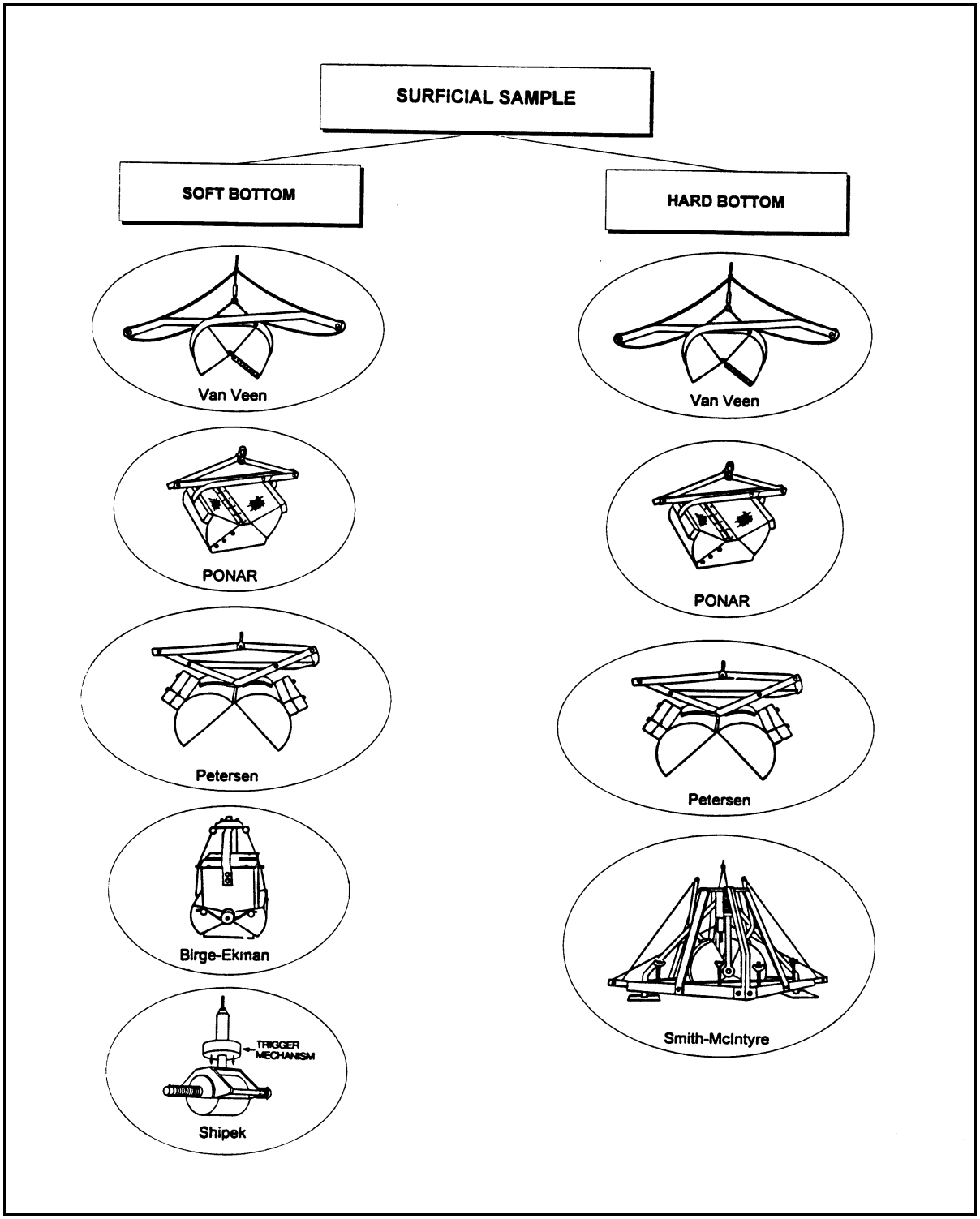

Figure E-1. Some recommended devices for collecting surficial sediments (drawings from Murdoch and Azcue 1995 and Fredette et al. 1990).

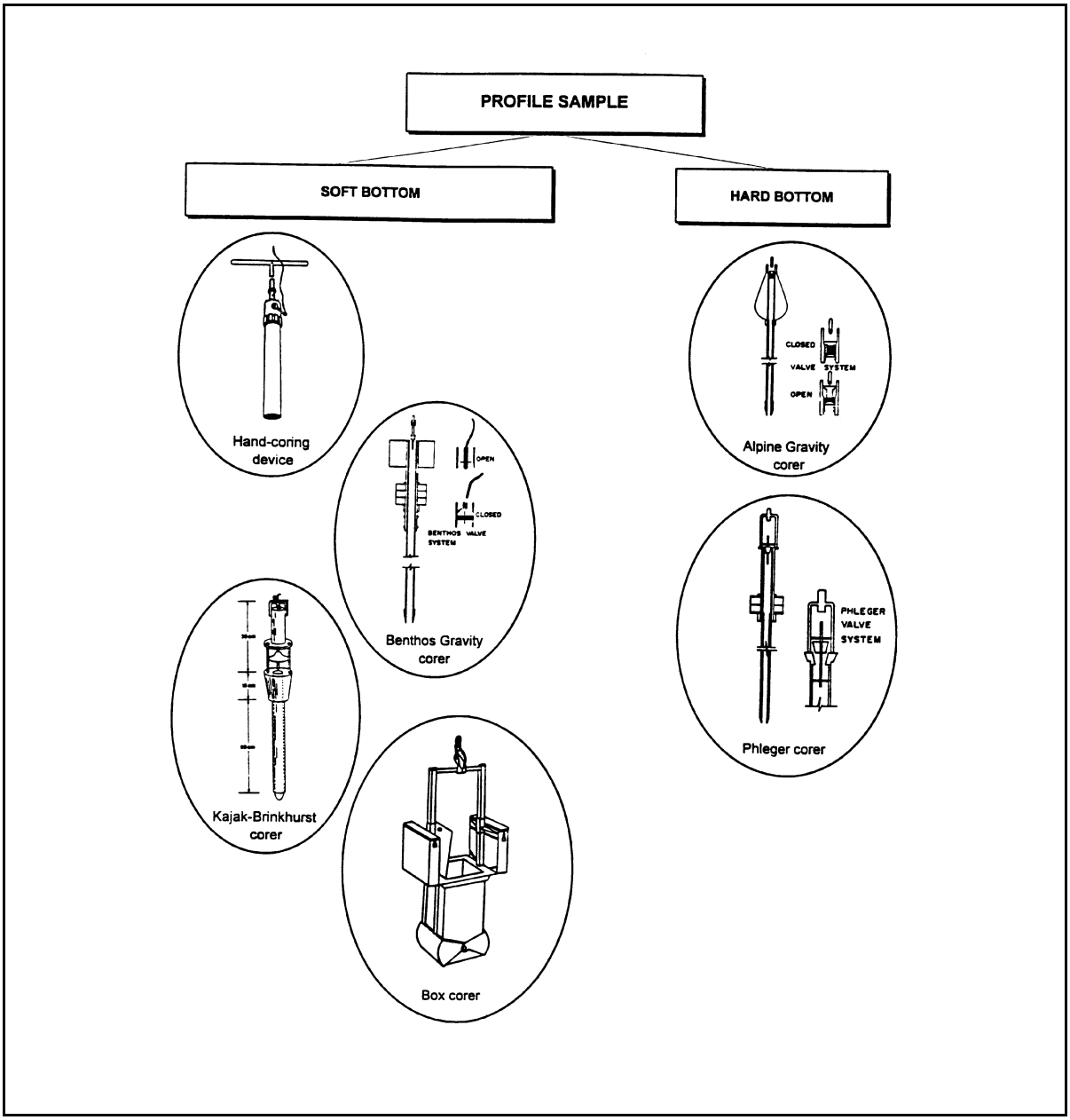

Figure E-2. Some recommended devices for obtaining sediment profiles (drawings from Murdoch and Azcue 1995 and Fredette et al. 1990).

APPENDIX F

EXAMPLES OF FIELD FORMS USED TO DOCUMENT STATION AND SAMPLE CHARACTERISTICS AND SAMPLE TRACKING

NOAA - Chesapeake Bay and Adjacent Tribs. Sediment Toxicity Study - Field Form

Strata	Site Number	Alternate		
Date		Time (local)		
ANALYSIS				
Metals	Organics	AVS	Chem-Grain Size	P450/microtox
Amphipod	Porewater	Benthos-comp.	Benthos-Biomass	Grain Sz&TOC
STATION LOCATION				
STATION COORDINATES				
GPS				
Latitude:	N			
Longitude:	W			
SEDIMENT DESCRIPTION				
Color:				
Texture:				
Odor/sheens:				
Benthic Organisms:				
WATER QUALITY				
Top			Bottom	
Temperature	Celsius		Temperature	Celsius
Salinity	ppt		Salinity	ppt
Dissolved Oxygen	mg/l		Dissolved Oxygen	mg/l
Conductivity	umhos		Conductivity	umhos
Water Depth	m or ft		Secchi Depth	m or ft
Sample Team				
OTHER COMMENTS				

Example of field form used by the Great Lakes National Program Office:

Field Sampling Log Sheet

Location and Core Information

Station Number:			**Water Surface Elevation**
Date			**Water Depth**
Time			**Core tube Length**
Primary GPS	**Latitude**		**Depth of Penetration**
	Longitude		**Length of Retrieved Core**
Secondary GPS	**Latitude**		**Loggers Initials**
	Longitude		**Samplers Initials**

Sample Intervals

Sample Number	Sample Interval	Physical Descritpion of Sample

Example of field form used for site remediation sampling at Naval bases:

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____ Sample ID No.: _____
Project No.: _____ Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date: / Time: / Method: / Monitor Reading (ppm):	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)

COMPOSITE SAMPLE DATA:

Date: / Method: / Monitor Readings (Range in ppm):	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

APPENDIX G

PHYSICO-CHEMICAL SEDIMENT CHARACTERIZATION

1. General Information

It is often necessary or desirable to determine certain physico-chemical characteristics of sediments in the laboratory, in conjunction with toxicity testing or chemical analysis for inorganic or organic contaminants. This characterization should include measurement of certain parameters known to mediate the availability of contaminants in sediment (ASTM, 2000f). Bulk chemical concentrations alone should not be used to evaluate bioavailability (USEPA, 1998). The following parameters are generally measured:

- pH (pore water)
- ammonia (pore water)
- total organic carbon
- particle size distribution (e.g., percent sand, silt and clay)
- percent water content
- salinity and hardness of pore water
- conductivity of pore water

Depending on the experimental design and/or study objectives, more extensive characterization may be necessary. Several additional characteristics which may assist in study implementation, data interpretation or QA/QC (i.e., assessing sediment integrity, artifact production, optimal extraction and test procedures) include: sediment biochemical oxygen demand (BOD), sediment chemical oxygen demand (COD), sediment oxygen demand (SOD), cation exchange capacity (CEC), Redox (Eh) or oxidation-reduction potential (ORP), total inorganic carbon, total volatile solids, acid volatile sulfides (AVS), simultaneously extracted metals (SEM), metals, synthetic organic compounds (pesticides, PCBs, PAHs, and TCDD-dioxin), oil and grease, petroleum hydrocarbons, dissolved organic carbon (DOC) in the pore water. Measurements of many sediment physicochemical characteristics use analytical techniques originally developed for soils and waters, and the literature should be consulted for details regarding recommended methodology (Black, 1965; USGS, 1969; Plumb, 1981; Page et al., 1982). The following sections provide rationale for making each type of sediment physicochemical measurement, along with brief descriptions of measurement techniques, and references for further information and specific procedures.

2. pH

Sediment pH is often one of the single most important factors controlling speciation and equilibria for many chemicals including sulfides, ammonia, cyanide, and metals, all of which ionize under the influence of pH. The USEPA ammonia water-quality criterion, for example, is dependent in part on pH because ammonia toxicity is largely governed by the unionized ammonia fraction which is pH-dependent (USEPA, 1999). Metal (Cd, Cu, Ni, Pb, and Zn) speciation and bioavailability are also known to be affected by pH (Schubauer-Berigan and Ankley, et al., 1991; Ho et al. 1999).

Generally, pH is measured using a pH meter consisting of a potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are submersed. General purpose process pH electrodes are available in a wide variety of configurations for in-line and submersion applications. Generally, electrodes with gel-filled references require less maintenance than electrodes with liquid-filled references. The latest instruments have microprocessors that automatically calculate and display the slope. Some older instruments have a percent-slope readout or (and) millivolt readout. For instruments with a millivolt readout, the measured electrode potential is calculated as the difference between millivolts measured at the known pH of two buffers.

Plumb (1981) and Gonzalez (1995) described a method for measuring pH in sediment using a pH probe and meter. The probe was inserted into the sediment and pH directly measured after at least a 5 minute equibration time. Electrodes have also been used for direct measurements of pH in sediment pore water, or in a 1 to 1 mixture of sediment to water (Jackson, 1958). Direct measurement of sediment pH is also possible using electrodes with "spear tip" designs allowing for greater penetration into the sample (Burgess, personal communication). Detailed methods for measuring pH in water and sediment are also described by USEPA (1983;1986b;1987), in USEPA (1979), and in USEPA (1987), respectively.

3. Ammonia in Pore Water

Nitrogen, a nutrient associated with over-enrichment of aquatic environments, exists in several forms, including ammonia. Ammonia is highly soluble in water where it is found in an un-ionized form (NH_3) and in an ionized form as NH_4^+. The extent of ionization is dependent on pH temperature, and salinity (in seawater). Ammonia in sediments and pore water is generally the result of microbial degradation of nitrogenous organic material such as amino acids (Ankely et al., 1990). Pore water concentrations of ammonia as high as 50 mg/L have been measured in otherwise uncontaminated sediments (Murray et al., 1978; Kristensen and Blackburn, 1987), while ammonia in pore waters from contaminated sediments can range from 50 to more than 200 mg/L (Ankley et al., 1990; Schubauer-Berigan and Ankley, 1991).

The toxic effects of ammonia are generally considered to be associated with the un-ionized fraction (NH_3) rather than the ionic components (NH_4^+ and $NH_4SO_4^-$), which co-exist in equilibria. This equilibrium is highly dependent on pH, temperature, pressure, salinity, and ionic concentrations of ammonia. The toxic un-ionized ammonia fraction can be calculated using known total ammonia values and measurements of pH, pressure, salinity, and temperature as described by Whitfield (1978) and Thurston et al (1981).

USEPA (1983), and APHA (1995) describe five methods available to measure ammonia in the pore water:

- the titrimetric method
- the ammonia-selective electrode method
- the ammonia-selective electrode method using known addition
- the phenate method
- the automated phenate method.

A preliminary distillation step may be required if interferences are present (APHA, 1995). Interferences, e.g., sample constituents that interact with procedural reagents, are described in detail in the APHA (1995) and ASTM (2000g) methods. Once distilled, the sample can be analyzed using any of the methods listed above.

The distillation and titration methods are frequently used when ammonia concentrations are greater than 5.0 mg/L. The ammonia-selective electrode method is appropriate when concentrations range between 0.03 and 1400 mg NH_3-N/L. Ammonia readings are calibrated against ammonia standards. To verify meter readings, confirmatory subsamples can be preserved and analyzed for ammonia using the standard Nessler technique described in APHA (1995). For the phenate method, APHA (1995) recommends distillation with sulfuric acid when interferences are present (Bower and Holm-Hansen, 1980). The automated phenate method is suitable for pore waters with ammonia concentrations in the range of 0.02 and 2.0 mg NH_3-N/L.

Hach Company, Inc. (Loveland, CO) describes the USEPA approved Nessler/distillation method adapted from APHA (1995). This is a photometric procedure and has been modified for use with Hach photometers.

4. Total Organic Carbon Content (TOC)

The total organic carbon (TOC) content of sediment is a measure of the total amount of oxidizable organic material. TOC is the sum of dissolved organic carbon (DOC), particulate organic carbon (POC) or suspended organic carbon (SOC), and colloids. TOC is an important parameter to measure in sediments because it is a major determinant of nonionic organic chemical bioavailability (DiToro et al., 1991). Metal bioavailability is also affected by the amount of TOC present in sediments. TOC is usually expressed as a percentage of the bulk sediment and is used to normalize the dry-weight sediment concentration of a chemical to the organic carbon content of the sediment. USEPA Equilibrium Partitioning Guidelines estimate bioavailability as a function of contaminant concentration sorbed to sediment organic carbon and contaminant concentration in the pore water under equilibrium conditions (USEPA, 1998). Recently, the presence of soot carbon from the combustion of organic carbon (e.g., fossil fuels) has been recognized as a fraction of the TOC in sediment. Soot carbon may alter the geochemistry and bioavailability of some organic contaminants (Gustuffson et al., 1997).

The organic carbon content of sediments has been measured using several methods including: wet oxidation titration, modified titration, and combustion after removal of carbonate by the addition of HCl and subsequent drying. USEPA methods(1986b; 1987), including SW-846 and 430/9-86-004, are often used to measure TOC. Plumb (1981) recommends one of two methods to separate organic from inorganic carbon before analyzing for TOC: (a) ignition and using HCl as the acid for pre-treating sediment, or (b) differential combustion, which uses thermal combustion to separate the two forms of carbon.

EPA/ACOE guidance (1998) recommends that TOC analyses be based on high-temperature combustion rather than on chemical oxidation, because some classes of organic compounds are not fully degraded by combined chemical and ultraviolet oxidation techniques. Inorganic carbon (e.g., carbonates and bicarbonates) can be a significant proportion of the total carbon in some sediments. Therefore, samples should be treated with acid to remove the inorganic carbon prior to TOC analysis. The procedure described by the Puget Sound Estuary Program (PSEP, 1997a) is recommended for TOC analysis because this method uses high-temperature combustion using an induction furnace. USEPA recommends a similar method using catalytic combustion and non-dispersive infrared detection (Leonard, 1991) for quantifying TOC.

U.S. EPA acknowledges that several methods for measuring the total organic carbon (TOC) content of sediments exist (See Nelson and Sommers 1996 for a review). However, acceptable methods must at a minimum include the following steps:

Sample Collection

- Sediment samples are collected and stored in non-organic containers

Sample Preparation

- Each sediment sample must have macroscopic pieces of shells (e.g., > 1 mm) removed and then be pulverized and homogenized

- Each sediment sample must be treated by direct addition with a strong non-oxidizing acid (e.g., HCL) for ~18 hours to remove inorganic carbon; sample pH should be ≤2 after acidification (Yamamuro and Kayanne, 1995)

- Each sediment sample must be oven dried following acid treatment (60 - 70° C) (Weliky et al., 1983; Yamamuro and Kayanne, 1995)

- Each sediment sample must be stored in a desiccator until analysis

- As noted, desiccation is highly recommended, however if not possible a pre- and post-acidification sample weight should be performed to correct for water uptake (Hedges and Stern, 1984).

Sample Analysis

- Each post-acidification sediment sample must be analyzed using acceptable instrumentation

- Instrumentation should have a detection limit of approximately 100 mg/Kg

- Quantification of organic carbon should be based on a sample's weight, measured before acidification.

Sample QA

A rigorous QA program should be in place to insure acceptable data quality, this may include:

- Performance of duplicate analysis on a subset of samples with the relative percent difference (RPD) between replicates below 30%

- Performance of analyses on certified standard reference materials (SRM) (e.g., NIST)

5. Particle Size Distribution (Percent Sand, Silt, and Clay)

Particle size is used to characterize the physical characteristics of sediments. Because particle size influences both chemical and biological characteristics, it can be used to normalize chemical concentrations and account for some of the variability found in biological assemblages (USEPA 1998) or in laboratory toxicity testing (USEPA, 2000d; Hoss et al., 1999). Particle size can be characterized in varying detail. The broadest divisions that generally are considered useful for characterizing particle size distributions are percentages of gravel, sand, silt, and clay. However, each of these size fractions can be subdivided further so that additional characteristics of the size distribution are determined (PSEP, 1996).

Particle size determinations can either include or exclude organic material. If organic material is removed prior to analysis, the "true" (i.e., primarily inorganic) particle size distribution is determined. If organic material is included in the analysis, the "apparent" (i.e., organic plus inorganic) particle size distribution is determined. Because true and apparent distributions may differ, detailed comparisons between samples analyzed by these different methods are questionable. Therefore, if comparisons among samples between studies is desired, sediment particle size should be measured using consistent methods (PSEP, 1996).

Sediment particle size can be measured by a number of different methods (Allen, 1975; Plumb,1981; PSEP, 1996; ASTM, 2000a). The best method will depend on the particle properties of the sample (Singer et al., 1988). Particle size distribution is often determined by either wet sieving the sample (USEPA, 1979; Plumb, 1981; PSEP, 1996; Singer et al., 1988), the hydrometer method (Day, 1965; Patrick, 1958), the pipet method (USGS, 1969; Rukavina and Duncan, 1970), settling techniques (Sandford and Swift, 1971), and X-ray absorption (Duncan and Lattaie, 1979; Rukavina and Duncan, 1970). The pipet method may be superior to the hydrometer method (Sternberg and Creager, 1961). Combinations of multiple methods may provide refined measurements of particle size distribution. Gee and Bauder (1986) used sieving and pipetting after soluble salts were removed. Gonzalez (1995) used a combination of sieve and hydrometer methods. Folk (1968) and Buchanan (1984) discuss additional methods to measure particle size.

Recommended methods for measuring sediment particle size distribution are those of PSEP (1996) and USEPA (1995). Percent gravel, sand, silt, and clay are determined as apparent distribution using a minimum sediment sample size of 100 g taken from a homogenized sediment sample (see Section 4.4). Organic matter should be removed prior to analysis by oxidation using hydrogen peroxide. Wet-sieving followed by dry sieving (mechanical shaking) separates the two coarse particle size groups. The silt-clay fraction is subdivided using a pipet technique that depends upon the differential settling rates of the two different particle size fractions. All fractions are dried to a constant weight. Cooled samples are stored in a desiccator and weighed.

To obtain an accurate determination of particle sizes for the fine fraction, the Coulter (particle size) counter method may be employed (McCave and Jarvis, 1973; Vanderpleog, 1981). This method gives the fraction of particles with an apparent spherical diameter. In a review of the available methods, Swift et al. (1972) found the Coulter counter method to be the most versatile method overall; however, it does not provide settling information. Another potential method for determining the particle size distribution of a very fine fraction is through the use of electron microscopy (Leppard et al., 1988). Collection techniques for very fine material can result in aggregation of larger colloidal structures (Leppard, 1986; Leppard et al., 1988). In general, particle settling methods are preferred to sediment sizing methods.

6. Percent Water or Moisture Content

Water content is a measurement of sediment moisture usually expressed as a percentage of the whole sediment weight. It is known to influence toxicity and is used to aid in the interpretation of sediment quality investigations. Sediment moisture content is measured as the difference between wet weight of the sediment and dry weight following oven drying at 50 to 105°C to a constant weight. Percent water is used to convert sediment concentrations of substances from wet-weight to a dry-weight. Methods for determining moisture content are described by Plumb (1981) and Vecchi (1999). Additional methods are provided in USEPA (1987).

7. Salinity of the Pore Water (Marine Sediments)

Salinity is a measure of the mass of dissolved salt in a given mass of solution. The most reliable method to determine the true or absolute salinity is by complete chemical analysis. However, this is time consuming and costly. Therefore, indirect methods are more suitable. Indirect methods include conductivity, density, sound speed, or refractive index (APHA, 1995). Salinity is then calculated from the empirical relationship between salinity and the indirect measurement. Conductivity measurements have the greatest precision, but respond only to ionic solutes (APHA, 1995). Density measurements respond to all solutes. APHA (1995) recommends the electrical conductivity method,

because it is sensitive and easily performed. APHA (1995) also recommends the density method, using a vibrating flow densitometer. USEPA (1986) methods should also be consulted.

A salinity refractometer can be used for quick readings of salt density in solutions such as sea water. These refractometers are easy to read, non-corrosive and lightweight. They have dual scales and an adjustable focus. Temperature and non-temperature compensating refractometers are available. Most refractometers are accurate to 1 ppt and read specific gravity (1.000 to 1.070 in .001 divisions) and parts per thousand (0-100 in 1 ppt divisions).

8. Conductivity of the Pore Water (Fresh Water Sediments)

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability is dependent on the presence of ions in the solution, the concentration of the ions, their mobility and valence, and temperature. Solutions of inorganic compounds are usually good conductors while those of organic compounds are usually poor conductors. Conductivity is enhanced by calcium, potassium, sodium, and magnesium chlorides and sulfides.

Meters can be used to measure the degree to which electrical current can travel through water. The unit of measure is 1 mS/m = 1 millisiemens/meter or 1 µS/cm = 1 microsiemens/cm. The reading indicates the amount of ions in the water. While traditional chemical tests for hardness measure calcium and magnesium, they fail to provide an indication of other ions (e.g., sodium). The conductivity meter provides a much better measure of ionic strength.

9. Acid Volatile Sulfide (AVS)

Measurement of acid volatile sulfides (AVS) and simultaneously extracted divalent metal (SEM) concentrations associated with AVS extraction can provide insight into the bioavailability of metals in anaerobic (anoxic) sediments (DiToro et al., 1990; Ankley et al., 1996). AVS is the reactive solid-phase sulfide fraction that is extracted by cold hydrochloric acid. AVS appears to affect the bioavailability of most divalent metal ions as the sulfide ions have a high affinity for divalent metals. This affinity results in the formation of insoluble metal sulfides with greatly reduced bioavailability. AVS concentrations in freshwater and marine sediments can range between < 0.1 and > 50 µmol AVS/g of sediment (DiToro et al., 1990).

The bioavailability of metals in sediments has been predicted by comparing the molar concentration of AVS to the molar concentration of SEM (methods described below). If AVS is greater than SEM, the metals are bound in sulfide complexes with greatly limited bioavailability. However, if AVS < SEM, metals may or may not be toxic due to other controlling factors (e.g., TOC).

The easily extractable sulfide fraction can be measured using the acid purge and trap technique. The sample sulfide is solubilized in cold hydrochloric acid. The analytical method involves conversion of sulfides to aqueous H_2S. This may be measured with a sulfide probe or by following a wet chemistry method. In the latter method, silver sulfide is precipitated in a gas-tight assembly and flushed with nitrogen to eliminate oxidation. The precipitate is filtered, dried, and weighed. The weight is compared with the weight obtained from a non-acidified sample, and the difference is attributed to the AVS fraction (DiToro et al., 1990).

10. Simultaneously Extracted Metals

A model for predicting toxicity from divalent trace metals (DiToro et al., 1990) is based on the binding of these metals to AVS. Where the sum of the moles of the SEM, including Ag, Cd, Cu, Ni,

Pb, and Zn is exceeded by the molar concentration of AVS, the metals are insoluble and largely unavailable to biota. The extraction of AVS and metals should be achieved using a single methodology to ensure that recoveries associated with each measure are consistent. Simultaneous extraction improves the efficiency of the methodology.

SEM can be measured in filtered aliquots by atomic absorption methods (DiToro et al., 1990). Recent SEM analysis methods use inductively coupled plasma atomic emission spectrometry (ICP-AES; Berry et al., 1999). Other methods for analysis of metals are described in Section 11 below.

11. Metals

Low levels of trace metals occur naturally in the environment but highly elevated levels in sediment are generally associated with anthropogenic contaminant loads. Metals are partitioned in sediments as soluble free ions, soluble organic and inorganic complexes, easily exchangeable ions, precipitates of metal hydroxides, precipitates with colloidal ferric and manganic oxyhydroxides, insoluble organic complexes, insoluble sulfides, and residual forms (Gambrell et al., 1976).

Current instrument methods available for the analysis of trace metals include electrochemistry (e.g., differential pulse polarography), spectrophotometry (e.g., silver diethyldithiocarbamate), atomic absorption spectrophotometry, atomic emission spectrophotometry, x-ray fluorescence (XRF), and neutron activation (PSEP 1997c). The most commonly used instrumental method to analyze sediments for metals is atomic absorption spectrophotometry (PSEP, 1997c). Inductively coupled plasma mass spectrometry (ICP-MS) or ICP-AES allow for simultaneous determination of many metals at sub-ppb levels with little pretreatment (Crecelius et al., 1987; Berry et al., 1999).

The concentration of salt in marine or estuarine samples may interfere with metals analyses (USEPA/ACOE, 1998). Therefore, acid digestion and atomic absorption spectroscopy should be coupled with an appropriate technique to control for this interference. Methods in USEPA (1986b) are recommended for the analysis of mercury in sediments and EPRI (1986) methods are recommended for the analysis of selenium and arsenic. EPA methods for cadmium, hexavalent chromium, copper, lead, mercury, nickel, selenium, silver, and zinc are described by USEPA (1986b). PSEP (1997c) suggests that mercury can be extracted using vacuum distillation and analyzed by gas chromatography/mass spectrophotometry.

12. Synthetic Organic Compounds (Pesticides, PCBs, TCDD-Dioxin)

Analytical techniques for measuring organic compounds require five general steps: drying the sample, extraction, drying the extract, clean up of the extract, and analysis of the extract. PSEP (1997b) recommends centrifugation or sodium sulfate to dry the sample and a solvent extraction, with application of shaker/roller, or sonication. Sample drying with sodium sulfate is recommended for samples weighing approximately 10 grams (after overlying water is decanted). The sediment and sulfate mixture is extracted and the extract is processed (MacLeod et al., 1985).

Soxhlet® extraction (USEPA, 1986b) involves distillation with a solvent such as acetone, dichloromethane/methanol (2:1), dichloromethane/methanol (9:1), and benzene/methanol (3:2). USEPA (1983) recommends sonication with solvent mixtures and a 30-gram subsample of sediment.

Drying the extract can be accomplished through separatory funnel partitioning as needed to remove water and sodium sulfate or by using a Kuderna-Danish apparatus and rotary evaporation with purified nitrogen gas for concentration to smaller volumes (PSEP, 1997c). Using the separatory funnel partitioning method, the wet sample is mixed with methanol and centrifuged. The supernatant

is decanted and extracted later. Extraction of the sample is continued using less polar solvents and the water/methanol and solvent extracts are combined and dried.

According to PSEP (1997c) elemental sulfur can be removed from the sediment sample with vigorous mechanical agitation using a Vortex or Genie® or using activated copper. Organic interferences can be removed with gel permeation chromatography (GPC) described in USEPA (1983), bonded octadecyl columns (PSEP, 1997c), high performance liquid chromatography (HPLC) described by Metro (1981), silica gel (PSEP, 1997c), or alumina (USEPA, 1983). Instrumental analyses for volatiles and semivolatiles and pesticides/PCBs are performed using gas chromatography/mass spectrophotometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD), respectively (PSEP, 1997b; Burgess and McKinney, 1997).

13. Oil and Grease

Oil and grease tests for sediments measure material recovered that is soluble in a nonpolar solvent under acidic conditions. Oil and grease compounds are substances such as hydrocarbons, vegetable oils, animal fats, waxes, soaps, and greases. Many solvents can dissolve other substances (e.g. sulfur compounds, organic dyes, and chlorophyll). Therefore, oil and grease is operationally defined by the solvent used and the analytical method used to perform the analysis. There are two basic methods used to analyze oil and grease: the gravimetric technique and the IR (infrared spectrophotometer) technique. Both are described by PSEP (1996).

14. Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons

Petroleum hydrocarbons are oil and grease constituents which remain in solution after contact with silica gel. Petroleum distillates, also called hydrocarbons or petrochemicals, refer to a broad range of compounds which are extracted by distillation during the refining of crude oil. During the fractional distillation of petroleum, crude oil is heated to allow various compounds to turn from liquid into gas and then captured as they rise, cool, and condense. Lighter, more volatile compounds rise higher before they condense and are collected on distillation trays. Heavier, less volatile compounds such as diesel fuel and oil are collected on lower distillation trays. Waxes and asphalts are collected from the bottom after the other products have volatilized.

Petroleum distillates contain both aromatic hydrocarbons (carbon rings) and aliphatic hydrocarbons (straight carbon chains). The chemical structure of the hydrocarbon largely defines the nature and behavior of these compounds. Aromatic hydrocarbons are the most toxic compounds found in petroleum products. Most aromatic hydrocarbons are chronic toxins and known carcinogens. Aromatic compounds are found in all crude oils and most petroleum products. Many aromatic hydrocarbons have a pleasant odor and include such substances as naphthalene, xylene, toluene, and benzene. Aliphatic hydrocarbons are flammable and may be explosively flammable. Aliphatic hydrocarbons include methane, propane, and kerosene.

Aromatic and aliphatic hydrocarbons were analyzed in sediments by Page et al. (1995a, b). Sediment samples were spiked with the appropriate surrogates, mixed with equal amounts of sodium sulfate to dry the samples, and extracted with a methylene chloride acetone mixture (Method 3550, USEPA, 1986b). The concentrated extracts were partitioned on an alumina column into saturated and unsaturated hydrocarbon fractions (Method 3611, USEPA, 1986b). The fractions were concentrated using the appropriate pre-injection volume, spiked with the appropriate internal standards, and analyzed by gas chromatography with flame ionization detection (GC/FID) and gas chromatography with mass spectrometry detection (GC/MS) operating in the selected ion monitoring (SIM) mode. The method of internal standards (Method 8000, USEPA, 1986b) using the average relative response

factors generated from the linear initial calibration was used to quantify the target compounds. All data were corrected for the recovery of the appropriate surrogate compound. Their relative abundances could then be used for identification and quantification purposes.

TPH (total petroleum hydrocarbons) and PAH (polycyclic aromatic hydrocarbons) have also been analyzed by first acidifying the sample with concentrated hydrochloric acid and then extracting hydrocarbons with a mixture of methanol and hexane. The hexane extracts were then spiked with an internal standard and analyzed by GC-FID for TPH content and by GC/mass spectrometry (MS) for PAH analysis.

Kaplan et al. (1996) extracted hydrocarbons using anhydrous Na_2SO_4 with methylene chloride and sonication. The total solvent extract was then concentrated with Kuderna-Danish equipment. The concentrate was further concentrated using a gentle stream of dry nitrogen. An aliquot was then injected directly into the gas chromatography.

15. Total Sulfides

Total sulfides represent the combined amount of acid-soluble H_2S, HS^-, and S^{2-} in a sample. Sulfides are often measured because they are common in some sediments, particularly those that are anoxic, and they can be toxic to aquatic organisms. PSEP (1996) describes a method to measure total sulfides in sediments. Oxygen is removed from the sample using nitrogen gas, methyl orange and hydrochloric acid is added, and the mixture is heated. Amine solution and iron chloride are added to develop a colorimetric reaction product and sample absorbance is measured spectrophotometrically.

Methods for measuring sulfides in aqueous samples include: potentiometric methods described by ASTM (2000e) and APHA (Method 4500, 1995). Sulfide ions are measured using a sulfide ion-selective electrode in conjunction with a double-junction, sleeve type reference electrode (Phillips et al., 1997). Potentials are read using a pH meter or a specific ion meter having a direct concentration scale for the sulfide ion. Samples are treated with sulfide anti-oxidant buffer which fixes the solution pH at a high alkaline level and retards air oxidation of sulfide ion in solution. This ensures that the sulfide measured represents total sulfides as $S^=$ ion and rather than the HS^- or H_2S found at lower pH values (see pH, Section 2 in this Appendix).

APHA (Method 4500, 1995) provides qualitative as well as quantitative methods to determine aqueous sulfide concentrations. Qualitative methods include the antimony test, the silver-silver sulfide electrode test, the lead acetate paper test, and the silver foil test. Quantitative methods include the photometric method, the automated photometric methylene blue colorimetric methods, and the iodometric titration method for standardizing stock solutions.

16. Sediment Oxygen Demand (SOD)

Sediment can exhibit significant rates of oxygen uptake attributable to either: (1) a benthic ecosystem supported by soluble organic substances in the water column, (2) naturally occurring sediments derived from aquatic plants and animals, and (3) detritus discharged into the water body by natural runoff. When numerical modeling is required to predict dissolved oxygen concentrations, the rate of dissolved oxygen consumed by the benthic ecosystem is defined as the sediment (benthic) oxygen demand (SOD) in g O_2/m^2-day.

Two approaches for measuring SOD were reviewed by Truax et al. (1995) including *in-situ* respirometry and laboratory respirometry methods. Numerous techniques have been developed for each approach. Generally, in-situ methods are considered more credible than laboratory

measurements although both apply the same technique. A given amount of sediment is enclosed in a chamber with a known water volume and oxygen uptake is measured over time. The SOD rate is then calculated based on the area of the enclosed sediment, the volume of water in the chamber, and the rate of uptake.

In situ sediment oxygen demand measurement method were described by Uchrin and Ahlert (1985). A cylindrical respirometer, a dissolved oxygen probe with stirring mechanism, and a dissolved oxygen meter were used. Ambient dissolved oxygen was measured using the probe/meter as well as by using the Winkler method (APHA, 1995) in the laboratory to determine the effect of respiration on total dissolved oxygen uptake. The respirometer was deployed in a level area at the bottom of the water body. Dissolved oxygen were recorded initially and at 15-minute intervals thereafter to determine the SOD rate.

17. Sediment Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is a measure of the dissolved oxygen consumed by microbial organisms while assimilating and oxidizing the organic matter in a sample (PSEP, 1996). The test is an empirical methodology in which standardized laboratory procedures are used to determine the relative oxygen uptake of environmental samples. The test measures the amount of molecular oxygen used during a specified incubation period to biochemically degrade organic material and to oxidize reduced forms of nitrogen (APHA, 1995).

Plumb (1981) described a method to analyze BOD in sediments using freshwater bacteria as a "seed" and buffered distilled water as dilution water. PSEP (1996) described an alternative procedure to analyze BOD in marine sediments using marine bacteria as the "seed" and filtered, oxygenated seawater as the dilution water. USEPA (1987) methods should also be consulted.

18. Sediment Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of organic matter content in a sample that is susceptible to oxidation by a strong chemical oxidant at elevated temperature and reduced pH. The test was devised to augment the biochemical oxygen demand test. Chemical oxygen demand can be related empirically to biochemical oxygen demand, organic carbon, or total volatile solids (PSEP, 1996).

PSEP (1996) described a method for analyzing sediment COD using a closed reflux/colorimetric method. DiChromate (Cr_2O_7) ions are used to oxidize organic matter to carbon dioxide and water and to provide oxygen. The dichromate ions remaining after the reaction are measured by titration and the amount of oxygen consumed is then calculated.

Four standards procedures for measuring COD in water are available in APHA (1995): the open reflux method, the closed reflux method, the titrimetric method, and the closed reflux/colorimetric method. USEPA (1983) methods for the colorimetric and titrimetric method are described in USEPA (1979). Semi-automated methods are described in USEPA (1993).

Hach (Loveland, CO) has modified the EPA approved dichromate reflux method and the reactor digestion method. The methods are photometric and are adapted for use with Hach photometers.

19. Cation Exchange Capacity of Sediments

Cation exchange capacity (CEC) is a parameter that provides information relevant to metal bioavailability studies (Black, 1965). Cations or positively charged elements (such as calcium, magnesium, hydrogen, and potassium), are attracted to negatively charged surfaces of clay and organic matter. There is a continuous exchange of cations between sediment and water. CEC is a measure of the sediment's ability to retain cationic elements. It is also a measure of clay activity and mineralogy, which is used to calculate mineralization rates, leaching rates, and to predict interactions with contaminants. The degree of CEC is dependent on the kind and amount of suitable surfaces such as organic matter and clay. High cation exchange capacities are associated with high clay contents and high organic matter and changes in CEC are typically associated with changes in organic carbon content and pH of the sediment. Organic matter generally supplies a greater number of exchange sites than clay particles.

Various methods have been recommended to determine bioavailable fractions of metals in sediments (Chao and Zhou, 1983; Crecelius et al., 1987; Kersten and Forstner, 1987; DiToro et al., 1990). CEC can be measured by treating samples with ammonium acetate so that all exchangeable sites are occupied by NH_4^+ ion, digesting the samples with sodium hydroxide during distillation, and titrating to determine the ammonium ion concentration. The amount of exchangeable cations are expressed as milliequivalents of ammonium ion exchanged (meq) per 100 g of dried sample. More detailed methods are provided in Bascomb (1964), Black (1965), Klute (1986), and USEPA (1986b).

20. Redox Potential (Eh) of Sediments

Redox (Eh) is a measure of the oxidation-reduction potential (ORP) of sediments. Measurements of Eh are particularly important for metal speciation and for determining the extent of sediment oxidation. Eh values below approximately -100 millivolts would indicate biologically important sulfide concentrations. Some trace metals form insoluble complexes with sulfides. These metal-sulfide complexes bind the metals in a form that is not bioavailable. Since free ionic metals are generally thought to possess the greatest toxicity potential, it is important to understand conditions which control binding dynamics, such as pH and Eh.

Potentiometric measurements of Eh using a millivolt reader can be obtained with a platinum electrode relative to a standard hydrogen electrode (Plumb, 1981). APHA (1995) does not recommend the standard hydrogen electrode as it is fragile and impractical. Instead, their method uses a silver-silver-chloride or calomel reference electrode. APHA (1995) recommends a graphite rather than platinum electrode for sediments. Once the Eh equilibrium is reached, the difference between the platinum or graphite electrode and the reference electrode is equal to the redox potential of the system. For a more detailed explanation on how to calculate the Eh potential see APHA (1995). Gonzalez (1995) also describes a detailed method that can be used to measure sediment Eh.

There are a number of problems associated with the accurate measurement and interpretation of Eh in sediments, particularly in marine sediments. Therefore, considerable attention should be paid to the use of proper equipment and techniques. Some of the problems identified by Whitfield (1969) and Mudroch and Azcue (1995) include measurement inaccuracy due to disturbance of the sediment sample during insertion of the electrode, instability and poor reproducibility of the measurements and differential responses of platinum electrodes under different environmental conditions. A comprehensive description of the limitations of sediment Eh measurement is beyond the scope of this document. Rather, it is recommended that published studies on the problems associated with measuring and interpreting sediment Eh be consulted before any attempt is made to measure these parameters in sediment samples (Berner,1963; Morris and Stumm, 1967; Whitfield, 1969; Tinsley,

1979; Bates, 1981). The recommended procedure for measuring pH and Eh in the field are described in detail in the table below**:**

Table G-1. General procedures for measurement of Eh in bottom sediments (from Murdoch and Azcue 1995).

Equipment and solutions used in the measurements: • A portable, battery-operated pH/Eh meter, batteries, and a power cord for recharging the meter. • Combination glass and platinum electrodes or other electrodes suitable for the measurements. • Plastic test-tube-shaped containers or other containers for storing the electrodes in solutions during transport in the field. • Commercially-available or laboratory-prepared pH buffer solutions (pH 4 and 7) in plastic bottles with lids. • Freshly-prepared solution for calibration of Eh electrode in a plastic bottle with a tight lid. • Freshly-prepared solution of saturated potassium chloride for storage of the electrodes. • Other solutions necessary for proper functioning of electrodes as outlined by manufacturers. • Distilled water and wash bottle for storing and rinsing the electrodes between measurements. • Several small and larger plastic beakers for holding solutions, rinsing electrodes, etc.. • Support stands, rods, clamps to secure electrodes in solutions and during measurements. • Large plastic containers for storage and transport of used buffers and Eh-calibration solutions. • Notebook and pens, soft paper tissue.
Preparation of equipment before the field trip: • Check batteries of the portable pH/Eh meter and replace/recharge them, if necessary. • Prepare calibration solutions. • Check and test the pH and Eh electrodes. • Mark the electrodes vertically at desired intervals for insertion into the sediment samples. • Store the electrodes according the manufacturers instructions. • Pack all equipment for transport to the field and take spare electrodes if available.
Measurements in the field: • Allocate a space where measurements will be carried out. Within this space, all equipment should be assembled, checked for proper functioning, and prepared for measurement of the first sample. • Place grab sampler and sediment cores with recovered sediment in such a way that they will remain steady without disturbing the sediment samples during the measurements. • Insert electrodes carefully into the undisturbed sediment samples to avoid any air. contamination, particularly around the Eh electrode. Care must be taken not to generate any open space between the electrode and the sediment. Proper insertion of the electrode without disturbing the sediment is the most important step in measuring the Eh. • Insert electrodes into the sediment to the depth marked. Switch the pH/Eh meter to the pH scale and the value recorded within 1 minute after inserting the electrode into the sample. Switch the meter to the mV scale for recording the Eh value. The potential usually drifts considerably over the first 10 to 15 minutes, and then stabilizes. After stabilization, record the mV value. In measuring Eh of sediments from waters with low ionic strength, such as most freshwater bodies, it is recommended to “acclimatize” the electrodes in the water prior to measurement, particularly the electrodes that were stored in saturated potassium chloride solution. This will reduce the drifting of the potential after inserting the electrode into the sediment. • Remove both electrodes, wash them with distilled water to remove all adhering sediment particles, and dry them gently with a soft paper tissue. • Calibrate the electrodes after each five measurements. The electrodes may need less frequent calibration if pH and Eh are being measured in a sediment core.

21. Total Inorganic Carbon

Inorganic carbon has been measured as a complement to microbial activity (Bregnard et al., 1996), to determine the fate of an organic contaminant in biodegradation studies (West and Gonsior, 1996), and to determine the % carbon unaccounted for in fate transport predictions of hydrophobic contaminants (Tye, et al., 1996). Often the total inorganic carbon (TIC) fraction in samples is many times greater than the TOC fraction and presents an interference in the measurement of TOC. There are several options to eliminate TIC interferences when trying to measure TOC. One option is to compensate for the IC interference by measuring total carbon (TC) and total inorganic carbon (see Section 4 in this Appendix). The difference between the two is the TOC.

TIC is determined by acidifying the sample to convert the inorganic carbon (i.e., carbonates, bicarbonates, and dissolved CO_2) to carbon dioxide. Carbon dioxide is purged from the sample and then detected by a non-dispersive infrared detector (NDIR) calibrated to directly display the mass of carbon dioxide measured. This mass is proportional to the mass of TIC. Other instrumentation for the analysis of TIC is described in West and Gonsior (1996) and Tye et al. (1996).

22. Total Volatile Solids (TVS)

Total volatile solids represent the fraction of total solids that are lost on ignition at a higher temperature than that used to determine total solids. Total volatile solids are used as a crude estimate of the amount of organic matter in total solids (PSEP, 1996). In this regard, total volatile solids are often measured instead of, or in addition to, organic carbon content.

Total volatile solids are operationally defined by ignition temperature. Total volatile solids content does not always represent the organic content of a sample because some organic material may be lost at the drying temperature and some inorganic material (e.g, carbonates, chlorides) may be lost at the ignition temperature. Because of the temperature dependence of total volatile solids, valid interstudy comparisons require the use of standardized drying and ignition temperatures (PSEP, 1996).

Total volatile solids measurements are generally made by igniting the sediments at 550 ± 10°C until a constant weight is achieved and reporting the percent ash-free dry weight (McLeese et al., 1980; APHA, 1995; Keilty et al., 1988a). Plumb (1981) and PSEP (1996) describe standard methods for determining the total volatile solid content of sediments. Additional methods are provided in USEPA (1987).

23. Dissolved Organic Carbon in Pore Water

Dissolved organic carbon (DOC) often consists of humic substances and is the fraction of the organic carbon pool that is dissolved in water and passed through a 0.45 µm glass fiber filter. DOC is an indicator of the chemically reactive organic fraction and accurately measures the dissolved organic load. Sediment pore waters can be rich in humic acids. Fifty to 90% of the pore water DOC can be colloidal which is a significant factor because organic chemicals will preferentially partition to pore water DOC (Resendes et al., 1992; Burgess et al., 1996).

Hermann (1996) and Gilek et al. (1996) measured DOC using a TOC apparatus and infrared detection of CO_2. Borga et al. (1996) measured DOC using atomic emission spectrometry (ECP-AES). The APHA (Method 5310, 1995) methods for total organic carbon which can be applied to the measurement of DOC are (a) the combustion-infrared method; (b) the persulfate-ultraviolet oxidation method; and (c) the wet-oxidation method. Adjustments for inorganic carbon interference may be required (see Section 21 in this Appendix).

24. Alkalinity and Hardness of the Pore Water (Fresh Water Sediments)

Alkalinity is defined as the acid-neutralizing (i.e., proton-accepting) capacity of water. It is the sum of all the titratable bases and a measure of the quality and quantity of constituents in the pore water that result in a shift in the pH toward the alkaline side of neutrality. The measured value may vary significantly with the pH end-point used. Studies have shown that effects of certain contaminants such as metals are influenced by alkalinity as it alters speciation and bioavailability.

APHA (1995) recommends a color-change titration method to measure alkalinity which is also described by ASTM (2000h). The sample is titrated with standard alkali or acid to a designated pH

and the endpoint is determined electrometrically or by the color change of an internal standard. In addition, ASTM (2000h) describes two additional methods: (1) a titration curve is developed to identify inflection points, a standard acid of alkali is added to the sample by small increments and pH is recorded after each addition, and the total volume of acid or alkali is plotted against the observed pH values; and (2) pH is determined, standard acid is added to lower the pH to 4.0 or less, the solution is boiled with hydrogen peroxide, and titrated while hot to the phenolphthalein endpoint or when cooled electrometrically with standard alkali to pH 8.2, the desired endpoint. The color-change titration method is most commonly used. Hach (Method 8202) has developed a portable water chemistry kit based on the APHA (1995) color-change titration method and an additional method using sulfuric acid with a digital titrator (Hach, Method 8203).

Hardness is the concentration of metallic cations, with the exception of alkali metals, present in water samples. Generally, hardness is a measure of the concentration of calcium and magnesium ions in water. Hardness is usually expressed as a calcium carbonate equivalent in mg/L. Like alkalinity, hardness alters speciation and bioavailability of certain contaminants particularly many metals.

AHPA (Method 2340, 1995) describes two methods to measure hardness: (1) the calculation method and (2) the EDTA titrimetric method. ASTM (2000i) describes the APHA (1995) EDTA titrimetric method. Calcium and magnesium ions in water are sequestered by the addition of EDTA. The endpoint of the reaction is measured by means of Chrome Black T[3], which is red in the presence of calcium and magnesium and blue when both are sequestered. APHA recommends the calculation method because it is more accurate. The method uses direct determinations of calcium and magnesium to determine hardness. Hach has developed portable water chemistry kits (Methods 8222, 8204, 8030, 8226, 8213, 8338, 8329) for a variety of hardness determinations using a spectrophotometer or titration methods with a decision tree for selecting the appropriate procedure. Three of the Hach methods (1992) were adapted from APHA (Method 2340, 1995): the buret and 0.020 N titrant method (8222); the ManVer 2 buret and 0.020 N titrant method (8226); and the buret titration method (8338). The APHA EDTA titration method is most often used.