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H.1 Introduction

Quality assurance (QA) procedures are necessary to ensure that data are collected in a scientifically valid manner. This section describes many of the more general QA procedures that should be considered when collecting and analyzing environmental samples as part of data collection and analysis during the Preassessment Phase of an NRDA involving an incident. These procedures are general in nature because they pertain to samples collected for most kinds of environmental variables. They include procedures that should be followed when samples are collected in the field and shipped to laboratories (Puget Sound Estuary Program, 1991).

The USEPA has developed four QA approaches in its QA program (USEPA, 1991). Category I projects (i.e., major discharges of oil) involve the most rigorous and detailed approach, while Category IV projects involves the least stringent approach. The trustees should use the approach, or some version of it, that most accurately reflects the intended use of the data and the type of work being conducted

H.2 Sampling Preparation

All members of the field team should thoroughly review the field survey plan, including QA criteria, before each sampling excursion. The plan should be checked for completeness and clarity of objectives. A complete plan should contain the following major elements:

- Identification of the scientific party and responsibilities of each member;
- Statement and prioritization of study objectives;
- Description of survey area, including background information and station locations;
- Identification of variables measured and required containers and preservatives;
- Identification of all sample splits or performance samples submitted with the survey samples;
- Brief description of sampling methods, including station positioning technique, sampling devices, replication, and any special considerations;
- Detailed sampling schedule, including time, date, and location of embarkation and debarkation;
- Storage and shipping procedures;

- Identification of laboratories to which samples should be shipped after completion of sample collection;

- Survey logistics requirements (e.g., on vessels should include laboratory and sample storage needs); and

- All special equipment needed for the survey (e.g., GPS unit, video camera, communication devices).

Study objectives and their prioritization should be understood by all members of the sampling team. This will ensure that if modifications of the survey plan become necessary in the field, their effect on the overall goals of the survey can be evaluated adequately. After the sampling plan is reviewed, contingency plans should be outlined. These plans should include potential problems and their solutions. To ensure that all required sampling equipment and supplies are available at the time of sampling, an equipment checklist should be constructed. Spare parts and backup supplies should be included in the inventory.

H.3 Documentation

It is important throughout any sampling and analysis program to maintain integrity of the sample from the time of collection to the point of data reporting. Proper chain-of-custody procedures allow the possession and handling of samples traced from collection to final disposition. Documents needed to maintain proper chain-of-custody include:

- Field Logbook - All pertinent information on field activities and sampling efforts should be recorded in a bound logbook. The field supervisor should be responsible for ensuring that sufficient detail is recorded in the logbook. The logbook should enable someone else to completely reconstruct the field activity without relying on the memory of the field crew. All entries should be made in indelible ink, with each page signed and dated by the author, and a line drawn through the remainder of any page. All corrections should consist of permanent line-out deletions that are initialed.

At a minimum, entries in a logbook should include:

- ♦ Date and time of starting work;

- ♦ Names of field supervisor and team members;

- ♦ Purpose of proposed sampling effort;

- Description of sampling sit, including information on any photographs or videos that may be taken.
- Location of sampling site;
- Details of actual sampling effort, particularly deviations from standard operating procedures;
- Field observations;
- Field measurements made (e.g., pH, temperature, flow);
- Field laboratory analytical results;
- Sample identification;
- Type and number of sample bottles collected; and
- Sample handling, packaging, labeling, and shipping information (including destination).

- Sample Labels - Labels must be waterproof and securely attached to the outside and/or placed inside each sample container (i.e., depending on the kind of sample) to prevent misidentification of samples. Labels must contain at least the sample number, preservation technique, date and time of collection, location of collection, and signature of the collector. Labels should be marked with indelible ink. Abbreviated labels may also be placed on the cap of each jar to facilitate sample identification

- Chain-of-Custody - A chain-of-custody record must accompany every sample set. Each person who has custody of the samples must sign the form and ensure that the samples and records are not left unattended unless secured properly.

- Custody Seals - Custody seals are used to detect unauthorized tampering with the samples. Sampling personnel should attach seals to all shipping containers sent to the laboratory by common carrier. Gummed paper seals or custody tape should be used so that the seal must be broken when the container holding the samples is opened.

H.4 Collection of Water Samples

Water samples should be collected through deployment of water samplers to the desired depth of sampling, rather than using pumps and tubing. With pumps and tubing, there is always the risk that oil droplets will adhere to the inside wall of the tubing and be released randomly, making collection of a representative water sample difficult. The most commonly used samplers are the Kemmerer, Van Dorn, Niskin, and Nansen samplers. Samplers should be teflon-lined or composed of stainless steel. Multiple water samplers can be fixed on a rosette frame so that several depths can be sampled during one cast or replicate samples can be taken at the same depth.

When collecting water samples, the best technique is to collect the sample directly in the sample container, rather than having to transfer the water from the sampler to the container. This technique will minimize the potential for loss of sample integrity due to adherence of oil droplets to the inside surfaces of the sampler. The sample container is attached to a weighted holder that has a spring-mounted teflon stopper that can be opened once the container has reached the selected depth. Some types of sample bottles are designed for deployment with the stoppers closed. For example, Go-Flo bottles have a pressure sensor that triggers the opening of the stoppers when the sample bottle reaches a depth of about 10 meters. When it is necessary to collect water samples where surface slicks are present, use of a close/open/close type of bottle is required.

When sampling in clean areas, standard water samplers can be used. Prior to deployment, the stoppers of water samplers are cocked open. At this step, it is critical that the stoppers and the interior of the sampler remain free from contamination. All members of the sampling team should avoid touching the stoppers and the insides of the sampler.

Once the sampler reaches the desired depth, it should be allowed to equilibrate with ambient conditions for 2-3 minutes before it is closed. It is recommended that at least two samplers be used simultaneously for each depth. A second sampler provides a backup to the primary sampler in case of malfunction. A second sampler also increases the volume of sample available for subsampling and rinsing. To ensure that all subsamples at a particular depth are collected from the same water parcel, it is essential that they all be taken from a single cast, such as through use of a rosette sampler. Multiple casts using a single water sampler cannot meet this objective.

Once the water sampler is brought on board the sampling vessel, the stoppers should be checked immediately for integrity of the seals. If a stopper is not properly sealed, water from the sampled depth may have leaked out during retrieval and been replaced by water from shallower depths. In such cases, the entire water sample should be rejected.

Because a visual inspection might not detect all leaks, an additional check on sampler function may be conducted when sampling in marine settings. This check involves comparing the salinity of the water sample with ambient salinity determined with a CTD (Conductivity-Temperature-Depth probe) deployed with the sampler. A significant difference between ambient salinity and the salinity of a sample or an inconsistency between the salinity of a sample and the salinity profile determined from water in the other samplers from the same cast are indications that a particular sample is invalid. Water samples for chemical analysis and toxicity testing may consist of a single grab sample or a composite collected over a specific period. Containers must be made of non-toxic materials such as Nalgene, high density polyethylene, or polypropylene, and should be new and thoroughly cleaned before use. In the field, containers should be rinsed with sample water at least three times before collecting the actual sample. Each container should be filled completely to exclude any air and sealed appropriately. All containers should be placed on ice as soon as possible. They should be kept cold (4°C) and dark, never frozen. If the sample is collected directly in the container, care should be taken to assure integrity of the sample label.

H.5 Collection of Subtidal Surficial Sediments

This section describes the procedures required to collect an acceptable subtidal surficial sediment sample for chemical analysis and/or toxicity testing. In the past, sampling crews were given relatively wide latitude in deciding how to collect samples. However, because sample collection procedures influence the results of all subsequent laboratory and data analyses, it is critical that samples be collected using acceptable and standardized techniques. Detailed methods are provided here because few groups routinely collect subtidal samples.

H.5.a Design and Operation of Sediment Samplers

The primary criterion for an adequate sampler is that it consistently collects undisturbed samples to the required depth below the sediment surface without contaminating them. An additional criterion is that the sampler can be handled properly onboard the survey vessel. An otherwise acceptable sampler may yield inadequate sediment samples if it is too large, heavy, or awkward to be handled properly. A common sampling device for subtidal surficial sediments is the modified van Veen bottom grab. However, various coring devices (e.g., box corer, Kasten corer) are also used.

Collection of undisturbed sediment requires that the sampler:

- Creates a minimal bow wake when descending;
- Closes to form a leak proof seal after the sediment sample is taken;
- Prevents sediment washout and excessive sample disturbance when ascending; and
- Allows easy access to the sample surface.

Most modified van Veen grabs have open upper faces that are fitted with rubber flaps. Upon descent the flaps are forced open to minimize the bow wake, whereas upon ascent the flaps are forced closed to prevent sample washout. Some box corers have solid flaps that are clipped open upon descent and snap shut after the corer is triggered. Although most samplers seal adequately when new, the wear and tear of repeated field use eventually reduces this sealing ability (i.e., through chipped or improperly aligned jaws). A sampler should therefore be properly maintained and monitored constantly for proper operation and minimal sample leakage. If unacceptable leakage occurs or the sampler malfunctions in any manner, the sampler should be repaired or replaced. If a sampler is borrowed or leased for a project, its operation and sealing ability should be evaluated prior to sampling. Further, it is prudent to have a backup sampler onboard the survey vessel if the primary sampler begins leaking during a cruise.

The required penetration depth below the sediment surface is a function of the desired sample depth. Generally, it is better to penetrate below the desired sample depth to minimize sample disturbance when the sampling device closes. Penetration depth of most sampling devices varies with the sediment character, greatest in fine-grained sediments and least in coarse-grained sediments. In both cases, penetration depth can be modified by adding or removing weights from the samplers. Thus, it is optimal to use a sampler that has a means of weight adjustment. If a sampler cannot consistently achieve the desired penetration depth, an alternate device should be used.

The sampler should be brought aboard the vessel with a minimum amount of swinging to minimize sample disturbance. Once the sampler is secured onboard the survey vessel, it is essential that the surface of the sample be made accessible without substantially disturbing the sample. Most samplers have hinged flaps on their upper face for this purpose. The openings in the upper face of the sampler should be large enough to allow convenient subsampling of the sediment surface. If an opening is too small, the sample may be unduly disturbed during subsampling.

The sampling device should be attached to the hydrowire of the vessel boom using a ball-bearing swivel. The swivel will minimize the twisting forces on the sampler during deployment and ensure that proper contact is made with the bottom. For safety, the hydrowire, swivel, and all shackles should have a load capacity at least 3 times greater than the weight of a full sampler. In addition, screw-pin shackles should have wire through the eye and around one side of the shackle to prevent the pin from rotating.

The sampler should be lowered through the water and retrieved at a controlled speed of approximately one foot per second. Under no circumstances should the sampler be allowed to "free fall" to the bottom, as this may result in premature triggering, an excessive bow wake, or improper orientation upon contact with the bottom. The sampler should contact the bottom gently, and only its weight or piston mechanism should be used to force it into the sediment.

H.5.b Sediment Sampling Interval

The upper 2 cm of sediment is recommended for analysis because that is the sediment horizon in which most infaunal organisms reside and the horizon that is contacted most frequently by epifaunal organisms. When collecting the upper 2 cm of sediment, it is recommended that a minimum penetration depth of 4-5 cm be achieved for each acceptable sample. The portion of sample below the upper 2 cm of sediment can be discarded after the surficial sediment is collected (unless the study design specifies otherwise).

Although the 2-cm specification is arbitrary, it will ensure that:

- Relatively recent sediments are sampled;
- Adequate volumes of sediment can readily be obtained to satisfy the needs of most study objectives; and
- Data from different studies (historical or ongoing) can be compared validly.

Sampling depths other than the upper 2 cm may be appropriate for specific purposes, or when baseline data are available for a different interval.

H.5.c Sediment Sample Acceptability Criteria

The sediment in the sampler should be inspected to determine if the sample satisfied the following acceptability criteria:

- The sampler is not overfilled with sample such that the sediment surface is pressed against the top of the sampler;
- Overlying water is present, indicating minimal leakage;
- The overlying water is not excessively turbid, indicating minimal sample disturbance;
- The sediment surface appears relatively undisturbed, indicating lack of channeling or sample washout; and
- The desired penetration depth is achieved (i.e., 4-5 cm for a 2-cm deep surficial sample).

If a sample does not meet all of these criteria, it should be rejected and discarded away from the sampling station.

H.5.d Sediment Sample Collection

After a sample is judged acceptable, the following observations should be entered on the field log sheet:

- Date and time
- Station location at the time of bottom contact
- Station depth

- Gross characteristics of the surficial sediment
    - ♦ Texture
    - ♦ Color
    - ♦ Biological structures (e.g., shells, tubes, macrophytes)
    - ♦ Presence of debris (e.g., wood chips, wood fibers, human artifacts)
    - ♦ Presence of oily sheen
    - ♦ Obvious odor (e.g., hydrogen sulfide, oil, creosote)
- Gross characteristics of the vertical profile determined after the surficial sediments are collected
    - ♦ Vertical changes in sediment characteristics
    - ♦ Presence and depth of any apparent redox potential discontinuity layer
- Penetration depth

Before subsamples of the surficial sediments are taken, the overlying water must be removed. The preferred method of removing this water is by slowly siphoning it off near one side of the sampler. Methods such as decanting the water or slightly opening the sampler to let the water flow out are not recommended since they may result in unacceptable disturbance or loss of fine-grained surficial sediment and organic matter.

Once the overlying water is removed, the surficial sediment can be subsampled. Only sediments not in contact with the sides of the sampling device should be subsampled. It is recommended that subsamples be taken using a flat scoop. This device will allow a relatively large subsample to be taken accurately to a depth of 2 cm. Coring devices are not recommended because they usually collect inadequate amounts of surficial sediment and therefore require repeated extractions to obtain a sufficient volume of material for analysis of conventional sediment variables. A curved scoop is not recommended because it does not sample a uniform depth or volume with depth. Because accurate and consistent subsampling requires practice, it is advisable that an experienced person perform this task. Finally, sample contamination during collection must be avoided. All sampling equipment (e.g., scoops, containers) should be made of noncontaminating material and should be cleaned appropriately before use. It is recommended that all objects coming in contact with the sample be made of glass, stainless steel, or PTFE (e.g., polytetrafluoroethylene such as teflon). To avoid contamination, all sampling equipment should be cleaned in sequence with site water, pesticide-grade acetone, and pesticide-grade methylene chloride prior to initial use and between use for each station. Methylene chloride should be allowed to evaporate prior to using the equipment.

H.5.e Sediment Sample Homogenization

Sediment from single samples or composites of multiple samples should be homogenized prior to collecting subsamples. Compositing and homogenization can be accomplished by transferring sediment to a clean glass or stainless steel bowl and thoroughly homogenizing by stirring with stainless steel spoons or spatulas until textural and color homogeneity are achieved. The contents of the bowl should be continuously homogenized as subsamples are taken to prevent potential settlement of larger particles. In addition, unrepresentative material (e.g., stones, wood chips, seagrass) should be removed at the discretion of the chief scientist and noted in the field logbook. The bowl and all utensils should be cleaned in sequence with site water, pesticide-grade acetone, and pesticide-grade methylene chloride between composites and kept covered with aluminum foil to prevent airborne or other contamination. The methylene chloride should be allowed to evaporate prior to using the bowl and utensils.

All samples should be preserved according to the test requirements. In most cases, the samples are packed in ice and kept cold (4°C) and dark. Samples for toxicity testing should not be frozen.

H.5.f Collection of Sediment Chemistry Samples

If sediment chemistry samples are being collected concurrently with sediment toxicity test samples, they should be collected from the same homogenized sediment sample to ensure that the toxicity and chemical results are related as closely as possible. Sample homogenization and removal of bioassay aliquots should be conducted so that chemical aliquots are not contaminated in the process. Recommended sample size for chemical analysis is about 100 grams (i.e., about one cup) and samples should be placed into clean glass jars with teflon or aluminum cap liners. Sediment samples for chemical analysis can and should be frozen as soon as possible.

H.5.g Replication of Samples for Toxicity Testing

Replicate analyses are conducted on toxicity test subsamples to assess the variability encountered in laboratory testing, rather than the variability of sediment toxicity that exists in the field. To assess field variability, an alternate sampling design could be specified that requires each test replicate to be run on a separate replicate grab sample from each station. The primary drawback to this technique is that the single set of chemical concentrations usually measured at each station would not relate directly to the sediment toxicity measured in each replicate grab sample. This lack of direct relationship between toxicity test and chemical results can sometimes make data interpretation difficult for individual replicate samples. However, the mean toxicity test response could be compared directly with the chemical concentrations if the chemical measurements are made on a composite of equal amounts of sediment subsampled from each of the replicate samples used for toxicity test analysis.

H.6 Collection of Intertidal Sediments and Soils

Collection of intertidal sediments and soil samples is relatively straightforward because the samples do not have to rely on a remote sampling device. Detailed methods for sampling are provided in USEPA (1984; 1989). Many of the components of sediment and soil sampling are similar to those discussed in the previous section. Key differences include:

- Sampling interval - usually the top 5 cm of sediment are collected, or visual observations are used to select intervals;
- Grain size variations can be very large, from clay to boulders, making the sample more heterogeneous and requiring more replicates or composites;
- The level of contamination can be very high, so extreme care must be taken to avoid cross contamination. New core tubes or sampling utensils should be used for each sample; and
- Sites should be photographed prior to the collection of samples.

H.7 Tissue Sampling

Tissue samples are collected for either chemical or histological analysis. Organisms analyzed for petroleum hydrocarbons should be freshly killed. Decomposed organisms are rarely of any value for analysis. Field documentation should include detailed descriptions of the oiling conditions of the site, location, elevation, etc. Each organism should be photographed prior to sampling. For example, when collecting molluscs, overview photographs to document the exact location and substrate and close-up shots of clusters prior to sampling are valuable.

All instruments used in handling samples must be made of a non-contaminating material (e.g., stainless steel, glass, teflon, aluminum). Whole small organisms may be stored in clean glass jars. Large or irregularly shaped organisms may be wrapped in solvent-rinsed aluminum foil, placing the organism against the dull side. Tissue sections may be taken either on site from freshly killed organisms or in the laboratory from carefully collected and preserved samples. New, clean, sharp scalpels are used for tissue collection from each animal. The stomach and intestinal tract should be collected last to minimize contamination. Recommended sample size is 10-15 grams. Samples for chemical analysis should be kept at 4°C.

Samples for histological analysis should be about the size of a walnut and kept cold or preserved in the field. All samples from the same organism can go into a single bag. Preserved samples should be fixed appropriately. Trustees should consult with a pathologist regarding sample preservation.

H.8 Sample Shipment

Samples of oil and oiled sediments may often fall under the category of dangerous goods, also known as hazardous materials. Special packing and shipping procedures are required when dangerous goods are being transported. The U.S. Department of Transportation (USDOT) and the International Air Transport Association (IATA) are two major groups that regulate the transportation of dangerous goods. It is assumed that responders will ship oil-related samples via Federal Express (FedEx). FedEx follows IATA (1995) regulations. Trustees are referred to the IATA regulations for sample shipment.

H.9 References

IATA. 1995. Dangerous Goods Regulations, 36th edition: IATA, Montreal, Quebec.

Puget Sound Estuary Program. 1991. Puget Sound protocols: U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, WA.

U.S. Environmental Protection Agency. 1984. Sediment sampling quality assurance user's guide: Environmental Monitoring Support Laboratory, Las Vegas, NV.

U.S. Environmental Protection Agency. 1989. Soil sampling quality assurance user's guide, Review Draft: Environmental Monitoring Support Laboratory, Las Vegas, NV.

U.S. Environmental Protection Agency. 1991. Preparation aids for the development of Category IV Quality Assurance Project Plans: EPA/600/8-91/005, Office of Research and Development, Washington, DC.