Washington State Department of Ecology

Spill Prevention, Preparedness, & Response Program

Standard Operating Procedure for Collecting Oil Spill Source Samples

Version 1.0

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SPL001

Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
12/2/2010	1.0	Final edits	all	Bill Kammin

Spill Prevention, Preparedness, & Response Program

Standard Operating Procedure for Collecting Oil Spill Source Samples

1.0 Purpose and Scope

1.1 This document is the Spill Prevention, Preparedness, & Response (Spills) Program Standard Operating Procedure (SOP) for collecting oil spill source samples.

1.2 Objectives – 1) To obtain samples of the original product(s) involved in an oil spill incident, for characterization, fingerprinting, and predicting fate and effects (via bioassays) of the spilled oil. 2) To maintain the integrity the spill source samples during sampling, transport, and storage.

1.3 The primary purpose for collecting oil spill source samples is to clearly identify the responsible party and assign liability for clean-up costs and natural resource damages. The source samples are compared to environmental samples to document violations of applicable laws and natural resource exposures. To assign liability, source samples must be carefully collected to prevent contamination and strict chain-of-custody must be maintained throughout collection, transport, and analysis.

2.0 Applicability

2.1 This procedure is based on protocols developed by Research Planning, Inc. (http://www.researchplanning.com/services/damage-assessment-restoration/) for NOAA for oil spill Natural Resource Damage Assessments (NRDA). The protocols were based on sampling and analytical methods developed for the National Status and Trends Program. These protocols are widely accepted and used by oil handling companies, consultants, and other trustees and should be used for all oil spill related sampling.

3.0 Definitions

3.1 NOAA – National Oceanic and Atmospheric Administration.
3.2 GC/FID – Gas Chromatograph/Flame Ionizing Detector
3.3 GC/MS – Gas Chromatograph/Mass Spectrometer

4.0 Personnel Qualifications/Responsibilities

4.1 Any Ecology employee expecting to collect oil spill-related samples must attend appropriate training from a Spills Program Sampling Specialist. Source sample collection can be conducted by any staff that have completed basic sampling training and have collected at least one field sample under the supervision of an experienced sampler. All Spills Program staff (including managers and administrative staff) are encouraged to attend basic sampling training. Due to safety requirements, at least two people are required for any field sampling and anyone that has taken the training, with or without field experience, can assist an experienced sampler.

5.0 Equipment, Reagents, and Supplies

5.1 Equipment

5.1.1 Source samples can be collected directly into the sample container, minimizing risks of contamination. Use a device which holds the container, such as a Wheaton grab sampler (holds a 1-L bottle strapped to a metal rod with the ability to unscrew the cap remotely) or a Volskom sampler (frame which holds the container is lowered on a rope). For black oils, these methods can be messy, coating the device and container with oil.

5.1.2 Other types of samplers for transferring to a container include: drum thief; coliwasa (narrow tube with positive end seal); bailer; bomb sampler; and air-driven metallic pumps.

5.1.3 Sampler material, in order of preference: glass; stainless steel; Teflon (there are inexpensive disposable models); and PVC (may contribute phthalates, but should not interfere with interpretation).

5.1.4 Under emergency conditions, a new metal (preferred) or plastic (a last resort) bucket can be used after cleaning.

5.1.5 Transfer samples to glass containers, certified-clean as organic-free (i.e., solvent rinsed), with Teflon-lined lids. Wide-mouth containers are easier to fill. As a last resort, use clean (new) "mason" jars; submit an unused and empty jar along with samples that can be used as a blank.

5.1.6 Paper, metal, or plastic funnels are useful when transferring samples. Clean prior to use.

5.1.7 GPS (set datum to WGS-84).

5.1.8 Digital camera.

5.1.9 Ice chests with wet or blue ice (preferably equipped with chain of custody security cables).

5.2 Reagents

5.2.1 Pesticide grade acetone and hexane for decontamination.

5.3 Supplies

5.3.1 Sample tags and labels
5.3.2 Field notebook
5.3.3 Chain-of-custody seals
5.3.4 Chain-of-custody forms
5.3.5 Nitrile disposable gloves
5.3.6 Ziploc bags
5.3.7 Paper towels

5.3.8 Stainless steel spoons or spatulas
5.3.9 Liquinox or equivalent soap
5.3.10 Aluminum foil
5.3.11 Cleaning brush
5.3.12 Distilled water

6.0 Summary of Procedure

6.1 Sample Collection Procedure

6.1.1 Safety is of greatest concern. Be aware of physical and chemical hazards at the site. Get a safety briefing before entering the area. Do not enter confined spaces unless they have been determined to be safe. Use recommended safety equipment and procedures.

6.1.2 Collect the source sample as soon as possible, even for potential releases. Collect the sample directly from the tank that is the source of the spilled oil if possible. Alternatively, collect the freshest sample of the spilled material even if it is from the water, shoreline, etc.

6.1.3 Collect the samples directly into the glass containers if possible or use an appropriate decontaminated sampling device and transfer the sample into glass containers. One glass container can be used to collect the sample by scooping or dipping, etc. and then the sample is poured into another container so the outside of the transport container is kept clean, reducing the chance of cross contamination.

6.1.4 Use an appropriately sized container. Small spills (less than 1,000 gallons) only require about 125 ml (4 oz., collect at least two samples in case one is compromised). One liter samples should be collected for large spills.

6.1.5 When the source is not known or when multiple tanks on a vessel need to be sampled, numerous samples may need to be collected to identify the source. Label each sample container uniquely and sequentially, whether it is a replicate or from different storage tanks on a vessel. For example, Spill Name NRDA Source Oil No. 1-2P-rep 1 would be the first sample collected, from #2 port hold, replicate #1.

6.1.6 After labeling, place each sample container in a separate Ziploc bag to reduce the chance of contamination should a container leak or break.

6.1.7 Fill out the chain-of-custody form, noting where each source sample was collected from, sampling device used, time/date of collection, size and container type, and sampler name. Record the same information in a field notebook.

6.1.8 Make special notation on the chain-of-custody form about any problems or observations during sampling, such as visual differences in samples from different tanks, presence of water in the sample, etc.

6.1.9 Immediately place all samples in cooler and keep at 4°C (do not freeze).

6.1.10 Use packing material, such as bubble wrap, around containers to prevent breakage.

6.1.11 Maintain strict chain-of-custody during sample storage and transportation.

6.1.12 If possible, ship source samples separately from environmental samples to reduce risk of cross contamination.

6.1.13 Petroleum samples can be held at 4°C in the dark for up to 3-4 months without loss of sample integrity, as long as there is no organic material or water present to serve as nutrients for bacterial growth.

6.2 Analytical Methods

6.2.1 Petroleum products are usually analyzed for fingerprinting purposes, so that the spilled oil can be differentiated from other petroleum sources. Chemical analyses for this purpose includes:

6.2.2 Hydrocarbon Identification (HCID). A GC/FID is used to analyze petroleum source and environmental samples to determine if they match, i.e. the source oil is the same as the oil spilled into the environment. When there is any doubt to the origin of a spill, some oils can be analyzed for bio-markers for confirmation.

6.2.3 Bio-markers, steranes and triterpanes. These compounds are highly resistant to degradation and have a unique distribution for each batch of oil (unique to a specific load of crude oil). Thus, they are valuable for differentiating among different sources of hydrocarbons. This analysis is a specialized method using GC/MS in the selected ion monitoring mode.

6.2.1.1 Polynuclear aromatic hydrocarbons (PAH). PAHs are used to characterize the spilled oil, monitor weathering, and predict toxicity. If PAHs are to be measured, it is important that the analytes include the alkyl-substituted PAH homologs, in addition to the standard PAH "priority pollutants." This method is referred to as Modified EPA Method 8270 (NOAA list), because the list of PAHs is expanded to include the alkylated homologs, using GC/MS in the selected ion monitoring mode.

6.3 Decontamination Procedure

6.3.1 Wash with soap (Liquinox or equivalent) and water (preferably hot), scrubbing all surfaces thoroughly with the cleaning brush. If the item being cleaned is heavily contaminated (oiled), this step should be repeated after washing to remove gross contamination.

6.3.2 Rinse with tap water and then distilled water.
6.3.3 Rinse with acetone.
6.3.4 Rinse with hexane.
6.3.5 Allow to air dry.
6.3.6 Wrap in solvent rinsed aluminum foil.

7.0 Records Management

7.1 Sampling Plan Template – Use this form as an aid for developing a complete and comprehensive sampling plan. This form is not required for developing a sampling plan, but provides ready access to guidelines and reminders.

7.2 Sampling Documentation Form – Use this form as an aid and reminder for recording complete and comprehensive sampling information, and provides a single place to record information for multiple samples.

7.3 Both forms are available at:
http://teams/sites/SPPR/response/trap/Sampling/Forms/AllItems.aspx (SharePoint)

7.4 or X:\Spills_Program\Response Section\TRAP-NRDA\Sampling\

7.5 Oil Spill Chain-of-Custody Form (ECY 050-42 (11/01))

8.0 Quality Control and Quality Assurance Section

8.1 There are no QA/QC requirements specific or unique to this procedure. Field splits should be avoided. If splits are requested, the samples should be submitted to the laboratory and the laboratory can be asked to split the samples. Typically, the laboratory will extract the samples and then split the extracts. The laboratory will usually provide splits directly to the requester or their laboratory. If field splits cannot be avoided, a single large sample should be collected, mixed thoroughly to ensure the sample is homogeneous throughout, and then transferred into two or more containers. Separate samples from a single source should not be collected as duplicate samples; these samples are replicates and can have significant variability between samples. Replicate samples can be collected with the goal of determining if there is any variability between field samples. Duplicate analysis of at least one of the replicates should be requested to determine the contribution of analytical variability.

9.0 Safety

9.1 Sample collection can present some unusual circumstances that could have equally unusual associated safety hazards. Samplers should consult with the Safety Officer or SOSC and review the incident safety plan or Hazard Assessment Worksheet (HAW) prior to developing a sampling plan so known hazards can be avoided. Samplers should also be aware that sampling will often take place in areas that may not be adequately addressed in the safety plan or HAW. If there is any question, then a separate HAW should be prepared prior to sampling. A Sampling HAW is available at: X:\Spills_Program\ Response Section\TRAP-NRDA\Sampling, that includes action levels appropriate for sampling various petroleum products. Some hazards that could be associated with sampling are:

9.9.1 Low areas that could collect fumes (vapors) or have reduced oxygen levels (confined space)
9.9.2 Higher concentrations of fumes at ground level where samples are collected
9.9.3 General water hazards when collecting samples on a shoreline or from a boat or dock, etc.
9.9.4 Increased risk of slips, trips, and falls
9.9.5 Traffic when sampling near a highway
9.9.6 Dangerous animals
9.9.7 Exposure to elements (hot or cold)
9.9.8 Eye damage from splashes or brush/branches

10.0 References

10.1 NOAA, 1993. Sampling and analytical methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Water Projects, 1984-1992. Volume IV, Comprehensive descriptions of trace organic analytical methods. Lauenstein, G.G. and A.Y. Cantillo (eds.). NOAA Tech. Memo NOS ORCA 71, Silver Spring, MD. 181 pp.