Washington State Department of Ecology

Spill Prevention, Preparedness, & Response Program

Standard Operating Procedure for Collecting Oil Spill Water Samples

Version 1.0

Author – Dale Davis
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Reviewer – Rebecca Post
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QA Approval - William R. Kammin, Ecology Quality Assurance Officer
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SIGNATURES ON FILE

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)
09-30-2011	0.1			

Washington State Department of Ecology

Spill Prevention, Preparedness, & Response Program

Standard Operating Procedure for Collecting Oil Spill Water 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 water samples.

1.2 **Objectives** – 1) To determine the concentration of oil compounds in the water column. 2) To determine the degree of oil weathering. 3) To document the extent of exposure of water-column organisms and validate toxicity models. 4) To maintain the integrity of the sample(s) during sampling, transport, and storage.

1.3 The main purpose for collecting oil spill quantitative water samples is to document the concentrations of oil compounds in the water column and exposure of natural resources to determine if the resources have been injured. To be legally valid, samples must be carefully collected to prevent contamination and strict chain-of-custody must be maintained throughout collection, transport, and analysis.

1.4 Three types of analyses are typically conducted for water samples collected for oil spills; Total Petroleum Hydrocarbons (TPH), Benzene-Toluene-Ethybenzene-Xylene (BTEX), and Polynuclear Aromatic Hydrocarbons (PAHs). Detection limits for TPH analyses are usually higher than those needed for aquatic injury assessment, but the cost of this analysis is much lower than the PAH analysis and TPH can be used to track oil weathering and map extent of exposure of water column resources if the budget for analyses is limited. BTEX are compounds in most petroleum products that are highly soluble in water and cause most of the acute toxicity, but also break down or evaporate quickly. PAHs are very persistent and cause most of the chronic toxicity, and are therefore the preferred analysis for NRDA injury assessment.

2.0 Applicability

2.1 This procedure is based on protocols developed by Research Planning, Inc. (http://www.researchplanning.com/services/nrda.html) 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
3.4 TRAP – Trustee Resource Assessment and Protection.
3.5 NRDA – Natural Resource Damage Assessment.
3.6 SOSC – State On Scene Coordinator

4.0 Personnel Qualifications/Responsibilities

4.1 Any Ecology employee that expects to collect oil spill related samples must attend appropriate training from a Spills Program Sampling Specialist. Oil spill water sample collection can be conducted by any employee that has completed basic and intermediate sampling training and has collected at least one quantitative field sample under the supervision of an experienced sampler. All Spills Program employees (including managers and administrative staff) are encouraged to attend basic sampling training. Due to safety requirements, at least two people are recommended 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 Samples should be collected in certified clean glass containers. Alternatively, new glass containers (such as Mason jars or uncertified jars) can be used if certified containers are not available, but at least one empty container should be submitted with the samples as a container blank. New plastic water bottles (bottles sold in stores containing drinking water) can be used as a last resort. At least one unopened bottle should be submitted with the samples as a blank.

5.1.2 Water samples can be collected directly into the sample container, minimizing risks of contamination. Water samples analyzed for HCID, TPH, and PAH are typically collected in narrow mouthed one-liter amber glass bottles with Teflon lined caps. BTEX samples are collected in 40 ml amber vials (VOA vials) with Teflon lined septum caps (fill three vials for each sample).

5.1.3 Subsurface grab sampler, with a cable to allow opening and closing the sampler while the container is submerged; necessary for collection of water samples at depth (typically 1 to 3 meters). Grab samplers require use of a specific type of bottle (not available from Manchester Laboratory).

5.1.4 GPS (set datum to WGS-84, Latitude/Longitude to decimal degrees).

5.1.5 Digital camera (synched to GPS time).

5.1.6 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 Develop a sampling plan. Identify the number and type of samples that are to be collected, the type of containers that will be used, and unique identifiers for each sample. Make a drawing of the area being sampled, including points of reference and the location of each site where samples are collected so the sites could be located later if necessary. Identify the sampling procedure(s) that will be used. Include any preservation techniques used for the samples, the type of analyses that will be done, and the laboratory that the samples will be sent to. The plan can be recorded in a field notebook or on a separate piece of paper; there is no required form or specific format that must be followed. Each plan will be different depending on the number and type of samples being collected and the complexity of sampling site.

6.1.3 Collect subsurface samples below the water surface; do not include any surface slicks. Sampling equipment MUST be deployed and retrieved in the closed position; this applies to sample jars lowered by hand. Open the sampler or un-cap the container only at the sampling depth; close the sampler or replace the cap on the container (keep the cap underwater while the container is filling) prior to returning the sampler or container to the surface.

6.1.4 For the BTEX samples, avoid any air bubbles in the 40 ml vials. After collection of the sample, invert the vial and check carefully for air bubbles. If any bubbles are present, re-sample.

6.1.5 On each trip, try to sample the control/least oiled areas first, then more contaminated areas. Clear surface slicks prior to deploying the equipment, but carefully so that the surface oil is not dispersed into the water column. Sweeping the area with sorbents is effective.

6.1.6 If collecting samples by wading in shallow water, try to collect samples in water at least two feet deep, collecting the samples from mid-column. Avoid disturbing bottom material and try to keep the mouth of the container at least six inches below the surface during sample collection. If sampling moving water like a stream, hold the sample container opening upstream of the sampler.

6.1.7 Label each container with an adhesive label directly applied to the container and with a paper tag attached to the container with an elastic band. Use a waterproof pen or marker to record the project or incident name, a station identifier, a unique sample identifier, the collection date and time, the sample type (BTEX, PAH, etc.), and the sampler's name or initials on each label. The adhesive label should be filled out and applied to the container prior to sample collection.

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

6.1.9 Immediately place all samples in cooler and keep at d6°C (do not freeze).

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

6.1.11 Fill out the chain-of-custody form; being sure to record all information for each sample. Record the same information in a field notebook and add specific information about where each sample was collected from, including latitude-longitude and a map if necessary. Also include the sampling devices used, container sizes and types, if any preservative was used, and sampler name.

6.1.12 Make special notation on the chain-of-custody form about any problems or observations during sampling, such as potential sources of contamination, etc.

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

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

6.1.15 Samples can be held at d6°C in the dark for up to 7 days without loss of sample integrity. TPH and PAH samples can be extracted within the 7 days and the holding time for the extract is 40 days. BTEX samples must be analyzed within the 7 days unless they are preserved with HCl, which extends the holding time to 14 days.

6.2 **Analytical Methods**

6.2.1 **Total Petroleum Hydrocarbons** (TPH). As the name implies, this analysis is used to estimate the total amount of petroleum hydrocarbons in a sample, but does not differentiate among petroleum, petrogenic, and biogenic hydrocarbons. TPH can be used as an inexpensive alternative to the PAH analysis to monitor weathering and document the extent of exposure, but is not adequate for providing the data needed to support calculation of toxic effects, and detection limits are usually not low enough for aquatic injury assessment. This analysis is called NWTPH-Dx (diesel extended range) at the Manchester Laboratory and a GC/FID is used to quantify all hydrocarbons other than gasoline range compounds. NWTPH-Gx is used to quantify total gasoline range hydrocarbons, but the sample collected for BTEX analysis can also be used for the NWTPH-Gx analysis (one sample, two analyses).

6.2.2 **Benzene-Toluene-Ethybenzene-Xylene** (BTEX). BTEX are compounds in most petroleum products, are highly soluble in water, cause most of the acute toxicity, and break down or evaporate quickly. BTEX samples are analyzed using purge and trap with capillary gas chromatography and a photoionization detector.

6.2.3 **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 (SIM) 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 **Procedure**:

6.3.2.1 Rinse with tap water and then triple rinse with distilled water.

6.3.2.2 Rinse with acetone.

6.3.2.3 Rinse with hexane.

6.3.2.4 Allow to air dry.

6.3.2.5 If item is not used immediately, 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 to provide 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)
or X:\Spills_Program\Response Section\TRAP-NRDA\Sampling\

7.4 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 the sample contains enough material.

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 that includes action levels appropriate for sampling various petroleum products is available at:
http://teams/sites/SPPR/response/trap/default.aspx (SharePoint) or X:\Spills_Program\Response Section\TRAP-NRDA\Sampling.

9.2 Some hazards that could be associated with sampling are:

9.3 Low areas that could collect fumes (vapors) or have reduced oxygen levels (confined space)

9.4 Higher concentrations of fumes at ground level where samples are collected

9.5 General water hazards when collecting samples on a shoreline or from a boat or dock, etc.

9.6 Increased risk of slips, trips, and falls

9.7 Traffic when sampling near a highway

9.8 Dangerous animals

9.9 Exposure to elements (hot or cold)

9.10 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.