

**PROCEDURES FOR COLLECTION, SHIPPING  
AND  
LABORATORY SUBMISSION OF SAMPLES**



**OFFICE OF SPILL PREVENTION & RESPONSE**

**PETROLEUM CHEMISTRY LABORATORY**

**DECEMBER 2016**

**Revision 14**

**California Department of Fish and Wildlife**

## Notice of Intent

Information in this manual is intended for use by field staff of the Office of Spill Prevention and Response (OSPR). It was prepared by staff of the Petroleum Chemistry Laboratory (PCL) for OSPR staff in collection of samples to be submitted to the PCL. While many of the procedures presented herein are applicable for use by other CDFW staff involved in deleterious material spill response, the specifics of sampling supplies procurement are applicable only to OSPR personnel.

All marine and inland petroleum samples should be submitted to the PCL at 1995 Nimbus Road, Rancho Cordova, CA 95670, telephone (916) 358-2803.

This manual is intended for use by OSPR staff only.

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## PROCEDURES FOR COLLECTION OF SAMPLES SUBMITTED TO PCL FOR ANALYSIS

California Department of Fish and Wildlife  
Office of Spill Prevention and Response  
Petroleum Chemistry Laboratory  
1995 Nimbus Road  
Rancho Cordova, CA 95670

### INTRODUCTION

Collection of samples during investigation of suspected pollution cases is crucial to the outcome of pollution investigations. Properly done, it produces samples which, when analyzed, can be of significant assistance to successful prosecution. Improperly done, it can lead to dismissal of an otherwise solid case. All procedural aspects of sampling are important: sampling equipment, sample collection, chain of custody, preservation, storage, and shipping. Our goal is to provide OSPR with a standardized method for sample collection. The procedures herein are those which, from our experience, yield results accepted by the courts. Use of these techniques will allow Petroleum Chemistry Laboratory (PCL) analysts to provide you with sound results.

### SAMPLING EQUIPMENT

Oil spill sampling supplies are available from the PCL as listed on page 15. As supplies are used up, requests for additional supplies should be addressed to the PCL via either telephone at (916) 358-2803, email, or mail addressed to OSPR Petroleum Chemistry Laboratory, 1995 Nimbus Road, Rancho Cordova, California 95670. Inland sampling kits are available upon request.

### CONTAINERS

Glass containers with Teflon lid liners supplied, or approved, by the PCL should be used for sampling petroleum products in water or soil whenever possible. Use of other containers could introduce interferences which have previously been eliminated by the Petroleum Chemistry Laboratory and could jeopardize the results.

## CONTAINER CLEANING

Containers supplied by the Petroleum Chemistry Laboratory have been selected specifically for petroleum hydrocarbon sampling. Potential interferences to the analyses performed at the PCL have been eliminated. Do not pre-clean these sample jars.

Do not re-use sampling tools unless they have been thoroughly chemically cleaned, or use disposable tools. Change outer gloves between samples if any direct handling of contaminated material has occurred. Use only those gloves which have been approved by the OSPR program and supplied by the PCL or OSPR Safety Officer. Other types of gloves may not provide adequate protection and could introduce contaminants such as waxes used on the outer surface of the glove which will interfere with the chemical analysis. After sampling, wipe down all jar exteriors and remove excess materials from rim of container to ensure a tight seal.

If circumstances dictate that non-standard containers or equipment must be used for sample collection, submit unused examples to PCL for identification of potential interferences.

## SAMPLE COLLECTION

Your initial observation can provide you with information necessary to determine the following:

- 1) Type of spilled material;
- 2) Type of sample to be taken (oil, soil, water, fish, vegetation, etc.);
- 3) Where to take samples.

Table 1 presents, in an easy to use form, guidelines for sample size, type of container and preservation for most types of samples you may encounter. This Table lists procedures for handling samples to be analyzed for petroleum hydrocarbons and total petroleum hydrocarbons (TPH).

## **SAMPLING LOCATIONS**

The area and extent of effect of a spill must be determined in order to achieve adequate reimbursement for damages. For sampling streams or rivers, a minimum of four samples should be taken. Sampling points should include:

- 1) SOURCE (in case of suspected point source pollution) if possible;
- 2) UPSTREAM (control sample) far enough to be out of the zone of influence of the point of entry and other possible points of entry;
- 3) POINT OF ENTRY to the stream or river; and
- 4) DOWNSTREAM, continuing downstream until no effect is apparent, to determine the extent of the oiled area.

The number of samples necessary for sampling shoreline or open water is variable. The sampling locations should include:

- 1) The SOURCE, when possible;
- 2) OTHER SOURCES of water flow into the affected area (control samples);
- 3) The suspected POINT OF ENTRY of the pollutant into the affected area; and
- 4) As many samples as is necessary to determine the EXTENT of pollution.

## **OIL SAMPLING**

Generally, oil samples should be taken from the surface of the water or substrate for identification or matching purposes.

Where neat or pure oil is available, collect a minimum of 40 mL of the oil in the jars provided. For a major spill response that will include extensive Natural Resource Damage Assessment activities, 1 Liter of source sample is appropriate.

Disposable wooden spatulas provided by PCL may be used to scoop up floating tar-balls, oiled debris or beached oil; either 8oz or 1.5oz jars may be used, depending on amount of sample collected.

Fiberglass cloth may be used to sample oil from surfaces of objects or sediments without disturbing underlying layers of previously existing contaminants.

## **NATURAL SEEP SAMPLING**

Collect a minimum of 5 grams or a maximum of 20 grams using a wooden spatula into a clean, 4 – 8 oz glass jar. Seal with Teflon lid liner. The sample collected, should be the freshest appearing part of the seep area. Cool immediately and transport to the Petroleum Chemistry Lab.

### **SOIL SAMPLING**

About 500 grams (1 lb.) of each soil sample should be taken in separate, clean, 8oz glass containers with Teflon lid liners.

### **OIL ON WATER SAMPLING**

If sampling oil on water, take 250 mL (8 oz jar) of surface water and oil, maximizing the amount of oil by skimming the surface. If only sheen is present, take a sample by floating 4 pieces of fiberglass cloth (3 x 12 inches) on the surface of the water. Pick up the strips with disposable wooden spatulas and place the cloth in an eight ounce jar and seal.

### **WATER COLUMN SAMPLING**

For TPH samples, submerge a sealed, inverted 1L bottle in the body of water to be sampled, remove the cap, turn it upright to fill displacing all air, reseal the bottle under the water surface, remove it from the water and wipe down its exterior prior to labelling.

For VOA samples, follow the procedure above with three 40mL VOA vials per sample, being sure to eliminate all air bubbles prior to capping.

Vertical water column sampling may be necessary in some situations: Consult your local field services biologist or call PCL for assistance, if necessary.

### **TISSUE SAMPLING**

New aluminum foil (heavy duty foil is preferable) should be used to wrap animal and plant materials to be analyzed for petroleum products. Wrap the samples with the dull side of the foil next to the samples. Foil-wrapped samples should be sealed in plastic bags and frozen as quickly as possible after collection.

For bird or mammal losses, coordinate sampling with Wildlife Operations. Samples of fur, feathers and/or organs as necessary should be removed with non-contaminating utensils and procedures, i.e. no plastic tools or containers. Use only new aluminum foil or the glass bottles provided with the sampling supplies.

In the case of fish losses, collect dying and/or fresh dead fish. Please do not send fish that have started to decompose, as this can influence the validity of analyses. If there is any question as to the quality of the sample, take the sample and then call PCL with any questions you may have. "A bird in the hand is worth two in the bush". Please send 6 whole fish of each major species involved, if possible, frozen in aluminum foil.

## LABELING

It is very important that jar and lid be labeled for each sample. This helps to ensure that no cross contamination or misidentification of samples occurs in the field or in the laboratory. Place the label on the exterior of the jar. Do not put loose labels inside the container. Use indelible ink to label the jar lid. For soil, vegetation or animal tissue samples, an alternative is to wrap the label in aluminum foil and place it inside the sample bag. This keeps the label legible and does not contaminate the sample.

Each sample container should be labeled on the exterior with your name, the exact sampling location, GPS coordinates if taken, date and time of collection, any preservatives used, and name of suspect, if any. Be sure to write in pencil or indelible ink since other inks tend to run when wet. Seal all containers with the evidence tape provided. Be sure to properly fill out the chain of custody section on the Form 1000 at time of collection.

## CHAIN OF EVIDENCE

To maintain sample integrity, a proper chain of evidence or chain of custody must be maintained. The chain of custody documentation space is located at the bottom of the Form 1000. All samples must be marked and appropriately identified to correlate with the chain of custody. The sampler or witness of sampling must be the first name on the Chain of Custody Form 1000. Each person accepting the samples is responsible for maintaining the chain of custody and ensuring that the Form 1000 is completely filled out. Failure to do so may jeopardize the admissibility of the evidence for court proceedings. The fewer persons there are in the chain, the better. The chain of evidence must remain with the item(s) at all times. *Samples will not ordinarily be analyzed without proper paperwork and chain of evidence.* Use a ball point pen and enough pressure to make all of the carbon copies legible. The Investigator/Sampler keeps the goldenrod copy.

## SAMPLE PRESERVATION

Samples with trace amounts of oil in water should be refrigerated immediately and transported to the PCL. Unrefrigerated storage in excess of 24 hours may invalidate the sample due to degradation. Samples where oil is obviously present should be refrigerated and transported to PCL as soon as possible. Samples of soil and tissue should be frozen and transported to PCL.



## SAMPLE STORAGE

All samples should be kept refrigerated or frozen depending on the type of material (see Table 1). Samples for prosecution should be kept secure under lock and key or in investigator's possession at all times.

## TRANSPORTATION OR SHIPMENT OF SAMPLES TO LABORATORY

Be sure to completely fill out form FG 1000, "**DFG Request for Analysis and Chain of Custody Record**". Please include the case Index/PCA assigned by the OSPR Cost Recovery Unit, a list of samples submitted for analysis, a map of collection sites as appropriate, and any other helpful information, including contact person and phone number. Also, any animals submitted for analysis must be accompanied by form FG 406, "**Initial Report of Fish and Wildlife Loss**".

The chain of custody must be properly and completely filled out, signed, and dated by each person receiving the item beginning with the sampler and followed by each person receiving and relinquishing the samples.

All samples should be kept refrigerated or frozen as necessary until just prior to shipment. Water, soil and vegetation samples should be shipped with blue ice and tissue samples should be shipped in waterproof containers and ice for cooling. Samples must be wrapped and sealed sufficiently to prevent intrusion of ice or water into the sample containers.

Be sure to include the Form 1000 in the shipping container; the chain of evidence documentation should always accompany the samples. Protect the form from staining or water damage with a zip lock bag. For all samples being transported to us by anyone other than yourself, be sure that you have sealed the sample containers with evidence tape and after sealing the outside of the shipping container, write your name across the tape seal. This will enable us to be positive that no one has tampered with the samples.

The best method of sample transportation is personal delivery. This makes determination of the chain of custody very easy. If you will be hand delivering the samples, call ahead to ensure that staff will be at the laboratory to accept the samples. Laboratory hours are 8AM-5PM Monday-Friday, closed week-ends and holidays. Arrangements may be made ahead of time if samples need to be delivered after normal business hours. Do not simply leave samples on the secretary's desk. They must be handed to an analyst so the chain of custody is maintained. For any other method of delivery, please arrange delivery during the previously stated laboratory hours.

For shipment of samples using Fed Ex, all current applicable state and federal shipping regulations

must be followed as well as current training of Shipment of Hazardous Materials offered by the California Department of Fish and Wildlife.

### WHERE TO SEND SAMPLES

Please send oil spill samples to the following address to the attention of the Staff Chemist:

Petroleum Chemistry Laboratory  
1995 Nimbus Road  
Rancho Cordova, CA 95670

Phone (916) 358-2803  
ATSS 8-434-2803  
FAX (916) 358-2801

Along with the samples, send any notes you have regarding suspected materials and types of activities going on in the area. A thorough field investigation can be very helpful to us in identifying the pollutant, and more importantly, can help you to put together a strong case. Also include a completed FG 1000, FG 406, sample listing, and sampling map if appropriate as mentioned in previous sections.

### CONCLUSION

We believe these guidelines will assist your investigation of marine oil spill cases and, if followed, will enable us to give you the best possible assistance in prosecution of violations of OSPR regulations and other applicable codes, laws and regulations.

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Table 1. Guidelines for sample size, preservation and holding times.

**Petroleum Hydrocarbon Confirmation, Characterization and Fingerprinting Comparison**

Method Reference:

1. ASTM Method D5739-06 Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry, modified.
2. EPA Solid Waste 846 Method 3500B, 3600C, 3650B, 3611B, 8000, 8260, 8270D, modified.

<b>Sample Type</b>	<b>Sample Size (minimum)</b>	<b>Container</b>	<b>Preservation</b>	<b>Holding Time</b>
Pure Oil (source)	40 ml	1.5 or 8 oz glass jar	Cool 4° C	NA
Water/Oil (moderate oil)	250 ml	8 oz glass jar	Cool 4° C	14 days
Water/Oil (sheen)	4 strips/ fiberglass	8 oz Glass	Cool 4° C	14 days
Sediment	500 g	8 oz Glass	Cool 4° C	14 days
Tar ball	250 – 500 g	8 oz Glass	Cool 4° C	NA
Vegetation (oiled)	1 pound	Aluminum foil	Freeze, - 20° C	6 months
Fish	6 Whole fish	Aluminum foil	Freeze, - 20° C	6 months
Feathers, fur	Enough for 0.2ml oil	Aluminum foil	Cool 4° C	NA

**These guidelines are presented to insure the best possible analytical results for petroleum hydrocarbon confirmation, characterization, fingerprinting comparison and total petroleum hydrocarbon analysis. Holding times are based on the possible presence of volatile components found in petroleum hydrocarbon crude oils and products which are subject to weathering by evaporation, biodegradation of the biomarkers as well as possible substrate decomposition.**

Table 1. Guidelines for sample size, preservation and holding times.

### Total Petroleum Hydrocarbon Analysis

Method Reference: EPA Solid Waste 846 Method 3500, 3550, 8000A and 8015, modified

Sample Type	Sample Size (minimum)	Container	Preservation	Holding Time
Pure Oil (source)	40 ml	1.5 or 8 oz. glass jar	Cool 4° C	NA
Water/Oil (moderate oil)	250 ml	8 oz. glass jar	Cool 4° C	14 days
Water Column (No visible oil)	1000 ml	1 L glass bottle	Cool 4° C	14 days
Sediment	500 g	8 oz. glass jar	Cool 4° C	14 days
Tar ball	250 – 500 g	8 oz. glass jar	Cool 4° C	NA
Vegetation (oiled)	1 pound	Aluminum foil	Freeze, - 20° C	14 days
Fish (oiled)	6 Whole fish	Aluminum foil	Freeze, - 20° C	6 months

### Volatile Organics Analysis (BTEX)

Water Column (No visible oil)	120 ml	3 x 40ml glass VOA vial	Cool 4° C	14 days
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**These guidelines are presented to insure the best possible analytical results for petroleum hydrocarbon confirmation, characterization, fingerprinting comparison and total petroleum hydrocarbon analysis. Holding times are based on the possible presence of volatile components found in petroleum hydrocarbon crude oils and products which are subject to weathering by evaporation and as well as possible substrate decomposition.**

## **TARBALL SAMPLE COLLECTION PROTOCOL**

### **For Beachwatch Volunteers**

Collect a minimum of 5 grams, and maximum of 20 grams. For a group of tarballs, collect enough samples to represent the area.

Using the tongue depressors as needed to pick up the tarball(s), collect the sample(s) into an 8 oz sample jar and seal with Teflon-lined lid.

Fill out and apply appropriate labels and seal the jar with evidence tape.

Using the Chain of Custody Request for Laboratory Analysis Form 1000, provide sample information including: Name of the collector; date and time of collection; description of collection site; latitude and longitude (if using a GPS); description of the sample when taken; description of sampling site conditions, e.g. weather conditions, numbers of tarballs in the area where the sample(s) were collected and any other pertinent information.

Deliver the tarball samples to:

California Department of Fish and Wildlife

Office of Spill Prevention and Response

Petroleum Chemistry Lab

1995 Nimbus Road

Rancho Cordova, CA 95670

915.358.2803

Rev 2

## MYSTERY SPILL SAMPLING GENERAL PROTOCOLS (FY13/14)

- For wildlife, once the threshold is reached for potential response to a mystery event (e.g., 2 oiled birds per day for 3 consecutive days in the same area), notify the Wildlife Response Coordinator (916.324.6715) and ask the responding OWCN member organization to take samples and send them to the PCL. It is important that this is done quickly once a threshold is reached.
- For tarball events not involving wildlife, it is up to the responding FRT members and the ODO to determine whether to submit samples for testing or not.
- If samples *are* to be tested, please notify the Cost Recovery Unit (916.322.4452) with sample collection date, location, etc. She will be tracking costs associated with this Index/PCA.
- Ship samples via FedEx to:
  - Dept. of Fish and Wildlife
  - Petroleum Chemistry Laboratory
  - 1995 Nimbus Road
  - Rancho Cordova, CA 95670
- Do NOT send shipments that would arrive on Saturday or Sunday. If samples are held over the weekend before shipping, they should be kept refrigerated and under appropriate security.
- The PCL's FedEx account number can be used if needed. It is: 1519-7630-1. If this account is used, call (916) 358-2858 to let the WPCL clerical know to which Index/PCA the bill should be charged.
- Enclose a "DFG Request for Analysis and Chain of Custody Record" with the shipment (see next page). This form should clearly show the species/matrix, location found, and date collected for each sample.
- Inform the PCL of the appropriate Index/PCA. For FY13/14 the mystery event Index/PCA is **6600/56247 Mystery Events**.
- The PCL, with input from the submitter and/or ODO, will name the event using the format "Mystery\_YearMonth\_County" using the year, month, and county of the first sample in the set. For example: Mystery\_2010November\_SLO. It will be up to the submitters and/or ODO to determine when a new event is occurring, but the same Index/PCA will be used for all mystery samples.

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**NATURAL SEEP SAMPLE COLLECTION**  
**FOR COMPLEX OIL SPILL EVENT**

Collect a minimum of 5 grams and a maximum of 20 gram sample.

Using a wooden tongue depressor as needed, collect a fresh portion of the oil sample into a clean glass sample jar and seal with a Teflon-lined lid.

Apply label identifying sample.

Using the Chain of Custody Request for Laboratory Analysis Form 1000, provide all relevant sample information. Include the following: date and time of collection, name of collector, description of collection site, name of the seep if it has one, gps coordinates and any other pertinent information to assist in the identification of the sample.

Deliver the seep samples to:

California Department of Fish and Wildlife

Office of Spill Prevention and Response

Petroleum Chemistry Lab

1995 Nimbus Road

Rancho Cordova, CA 95670

916.358.2803

Revision 1

December 2016

## Sampling Supplies

Nitrile Gloves, Blue, heavy-duty: S, M, L, XL

Nitrile Gloves, Purple, light-weight: S, M, L, XL

Jars 1.5 oz. (48/case)

Jars 8.oz (24/case)

Bottles 1.0 Liter, wide-mouthed amber (12/case)

VOA Collection Vials 40mL (72/case)

Tongue Depressors (1200/case)

Thermometer

pH Strips

Fiberglass Tape

FG 1000-DFG Request for Analysis and Chain-of-Custody Record (25/pkg)

Labels, small sample jars (100/pkg)

Labels, large sample jars (100/pkg)

Evidence Tape, large and small

Evidence envelopes FG 902 (May substitute plain white envelopes\* sealed with evidence tape)

Shop Towels\*

Aluminum foil\*

Zip-lock plastic bags\*

*All sampling supplies may be obtained from the Petroleum Chemistry Laboratory (PCL) when sampling for cases to be analyzed by PCL (except items with \* which must be purchased individually).*

*Revised August 2013*



## Sampling Plan Template

draft/final rev

date:

prepared by:

### TITLE

**SCOPE AND APPLICATION** -- Identify the purpose of sample plan and the particular concern which incurred the sample plan development

**Sampling Goals** -- State the goal of the sample plan. Provide an overview of the plan which will include a general statement of the number of samples, the area where the samples will be collected, and how this will be accomplished logistically. Include the types of analyses which will be performed, as this will determine how the samples will be collected, preserved and shipped.

**Project Organization and Responsibilities** -- Identify the agency in charge of the sample plan and person responsible for sampling only if the responsible party is not coordinating the activity. If the responsible party is coordinating this activity, identify the contact person as well as the person responsible for the actual sampling. This could include a contract consultant as well.

**Sample Locations and Schedule** -- Make a statement of where the samples will be taken. Include a detailed description of the locations as well as how this will be documented in the field during the activity. Include a diagram.

**Field Sampling Methods** -- Describe in detail how the samples will be collected. If field compositing methods will be used, describe the procedure. Describe field preservation techniques, if any, employed during the activity.

**Field Documentation and Sample Custody** -- For the Department of Fish and Wildlife, field documentation will be made on a form 1000, Request for Laboratory Analysis. Standard California Department of Fish and Wildlife chain-of-custody procedures will be followed. Should the responsible party be coordinating this activity, describe the appropriate documentation and chain-of custody procedures which will be used.

**Field Duplicates** -- Field duplicates will be prepared as a check on analytical procedures. Field duplicates are samples of materials collected in the field from the same location, at the same time, and analyzed for the same constituents. They are used to test the consistency of the sampling method and precision of the laboratory. At a minimum, one field duplicate will be prepared for every 10 samples submitted to the laboratory (10%). Duplicates will be labeled so that the laboratory is unaware of their identity as duplicates (blind duplicates).

**Equipment Rinsate Blanks** -- Equipment to be employed in the field to collect samples will be replaced or cleaned according to decontamination procedures between samples. Equipment rinsates of the final rinse of the sampling equipment will be collected before the first and after the final sample has been taken. Additional rinsate samples between samples will be taken if

necessary. Rinsate samples are used to determine if contamination has been introduced between samples and to assure that decontamination procedures are adequate. If contamination has been introduced, rinsate blanks will be used to isolate the samples contaminated.

**Decontamination Procedures** -- In order to avoid cross-contamination sampling, sampling materials shall be thoroughly cleaned between each sample using Alconox. After vigorous soaping of all portions of the sampling apparatus with a brush, the apparatus shall be triple-rinsed with distilled water.

**Trip Blanks** -- Trip blanks are intended to evaluate contamination introduced by sample preservation, transportation, storage, and analysis. Trip blanks are normally used for liquid samples. Trip blanks originate from the point of departure of all sampling material and are to be handled and analyzed as collected field samples.

**Field Sample Splits** -- Field sample splits are samples of the same materials collected in the field from the same location, at the same time, and analyzed for the same constituents, but sent to another laboratory. One sample is collected and split in the field after complete homogenization. Field sample splits are collected at a minimum of one for every ten samples or 10%. Field sample splits may be used to test the consistency of the sampling method, the precision of the laboratory and the reliability of the analytical method.

**Chemical Analysis to be Performed** -- Identify the chemical analysis to be performed by title and EPA method number in consultation with (PCL) analyst.

**Health and Safety** -- General health and safety guidelines will be followed as indicated by the Incident Action Plan.

#### Method References

1. Test Methods for Evaluating Solid Waste Physical/Chemical Method, SW846, Chapter 9, Chapter 12, Revision 0, September 1986

Prepared by:  
Susan Sugarman  
Revision 12 August 2013

Signature Page  
date submitted:

Prepared by: (Planning, NRDA, Response, etc.)

**Title of Sample Plan**

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Responsible Party, representative Date

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California Department of Fish and Wildlife representative Date

Approval

Incident Command

---

Responsible Party Date

---

Federal On-Scene Commander Date

---

California Department of Fish and Wildlife representative Date

# APPENDIX