STANDARD OPERATING PROCEDURE

Procedures for Collecting Water and Sediment Samples for Pesticide Analysis

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KEY WORDS

Field sampling; surface water; runoff; amber bottle; Mason jar; trowel

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1.0 INTRODUCTION

1.1 Purpose

This Standard Operation Procedure (SOP) describes commonly used procedures and methods Surface Water (SW) staff use for collecting ambient surface water and sediment samples to determine pesticide concentrations. Ultimately, the data collected will help identify potential risks of pesticide uses and to develop mitigation strategies to fulfill the Department of Pesticide Regulation's (DPR) mission of protecting the aquatic environment in the state's surface waters. The purpose of this SOP is to provide consistent and quality-assured procedures for collection of representative ambient surface water and sediment samples for pesticide analysis. This SOP replaces the older DPR SOPs FSWA002 (water sampling) and FSWA016 (sediment sampling) (Bennett, 1997; Mamola, 2005). Sample collection for trace metal analysis in marine environment require specific procedures and tools; refer to Study 319 protocol (Burant, 2019).

For the purpose of this document, surface water is defined as inland freshwater on top of the ground such as rivers, streams, creeks, canals, lakes, reservoirs, wetlands, municipal storm drains, and agricultural ditches. Sediment is defined as a mixture of fine organic and inorganic materials deposited on the bed layer underlying surface water.

2.0 MATERIALS

A generic checklist for equipment and supplies is presented below. Other supplies may be needed for specific projects.

2.1 Sample Containers

- Amber glass bottles (narrow mouth) with a Teflon sealed lid (various sizes, e.g., 0.5-L, 1-L)
- Certified pre-cleaned 1-L amber bottles (narrow mouth; e.g., I-CHEM 200)
- Wide mouth Mason jars, various sizes (1/2 pint, 1 pint, 1 quart)
- Airscape® 64 ounce stainless steel canister

2.2 Sampling Tools

- Extendable sampling pole (example, NASCO swing sampler)
- Stainless steel bucket
- Rope and carabiner or spring snap
- Stainless steel shovel
- Stainless steel trowel
- Stainless steel spatulas for sediment sampling
- Autosampler (e.g., Teledyne ISCO 6712)
- Peristaltic pump
- WILDCO Kemmerer water sampler (various volumes)

2.3 Meters

- Water quality meter
- Flow meter

2.4 Safety and Personal Protection Equipment

- Gloves, various (disposable, 18 or 26 inch Nitrile gloves)
- Rubber boots
- Headlamps/flashlights/lanterns
- Traffic cones
- Reflective vests
- First aid kit

2.5 Cleaning and Other Supplies

- Two 20-L carboys filled with DI water and tap water
- Plastic squirt (wash) bottles
- Ice chest
- Sandbags

2.6 Paperwork

- Field data sheets
- Chain of custody (COC) forms
- Laboratory check in sheets

3.0 PROCEDURES

General steps for sampling:

Step 1
- Notify lab liaison of sampling date, analyte screens, and number of samples

Step 2
- Prepare for sampling: label sampling bottles; print out paperwork

Step 3
- Locate sampling sites: print out or create an electronic file with site addresses and coordinates; plan sampling route with considerations of site location and traffic

Step 4
- Bag ice, calibrate water quality meter, load vehicle with equipment and supplies. Determine autosampler program if collecting time or flow weighted samples

Step 5
- Collect samples; complete field data sheets

Step 6
- Transport and store samples

Step 7
- Complete Chain of Custody Form and Sample Check-in Sheet

Step 8
- Clean and replace equipment

3.1 Grab Water Sample Collection

3.1.1 Choose collection sites per project protocols

3.1.2 Parking

Upon arrival at monitoring site, park vehicle on solid surface. If parking alongside a roadway, turn on the emergency flashers, set out traffic cones, and put on reflective vests.

3.1.3 Site observation

Observe the flow condition and prepare for collection when water is flowing. Ponded waterbodies are not recommended for sample collection.

3.1.4 Collecting samples

Put on appropriate gloves; rubber boots may be warranted at muddy sites or when wading or other personal protective equipment.

Pull out pre-labeled amber sampling bottles for specific site. Collect samples by submerging sampling bottles by hand or a sampling pole. Partially fill each with the water to be sampled by hand or using an extendable sampling pole designed to collect water samples directly into bottles (Figure 1). Rinse bottles by shaking or swirling, then drain the rinsate downstream or along streambank. Rinse once for chemistry samples or three times for toxicity samples. Use certified pre-cleaned bottles for toxicity samples.

Where possible, collect samples near stream center by submerging sampling bottles less than 0.3 m below water surface. Fill completely, if possible, with no air gap in the bottle neck. Avoid collection of aquatic macrophytes in sampling bottle. Cover the sampling bottles tightly with lid.

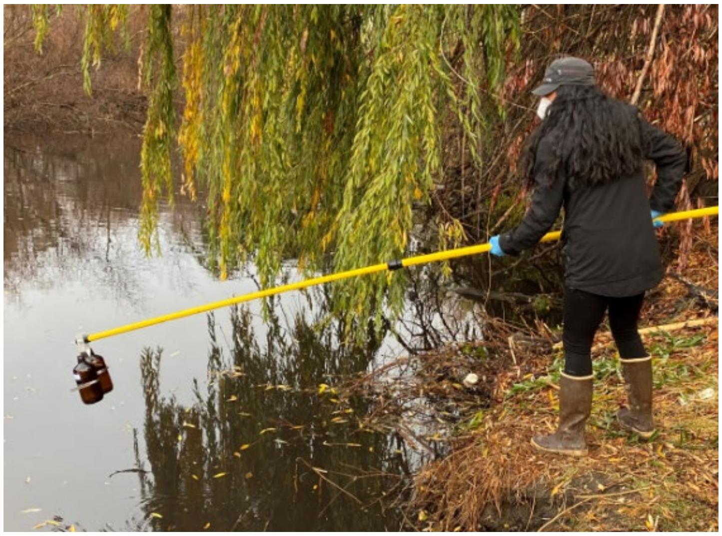


Figure 1: A sampling pole used in grab sampling

For shallow waterbodies where submerging sampling bottles is impossible, consider damming the waterways with sandbags to raise the water level, using a shovel to create a sink deep enough to submerge a sampling bottle, use of a stainless steel secondary container (Figure 2), or the grab function on an autosampler to collect the sample. Avoid stirring up bed sediments when sampling, especially when collecting samples in shallow waters. Ensure the use of collection device such as a secondary container does not come in contact with the sample containers. If wading to get to a sample site, approach the site from downstream and ensure flow clears sediment debris.

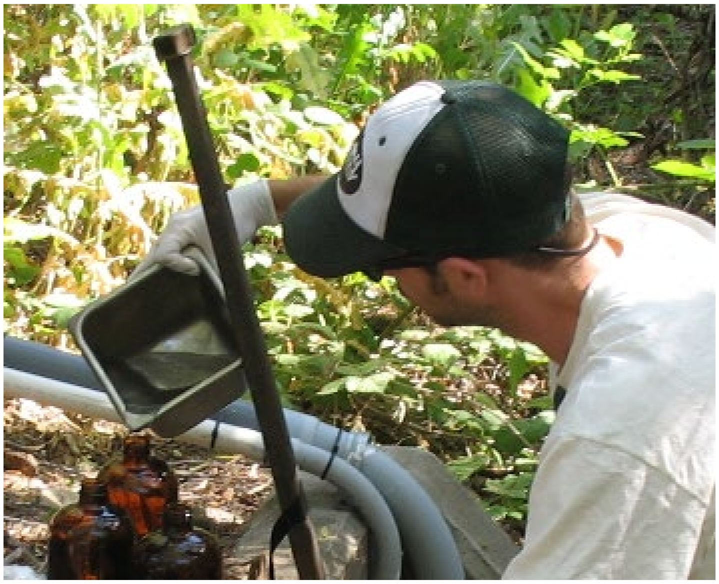


Figure 2: A stainless steel secondary container used in sampling shallow waters

3.1.5 Preservation

Some water samples may need acidification to prevent degradation of the analyte, e.g. carbamate insecticides (oxamyl, carbaryl, methiocarb). Samples can be acidified to pH <4 by adding 9.5 grams of potassium citrate to 1-L water samples (USEPA, 2001). Weigh potassium citrate into vials in the lab. After collecting a 1-L water sample in the field, add the citrate, and swirl bottle to mix.

Water samples for pyrethroid analysis need to be preserved with hexane to prevent degradation if the samples cannot be extracted within the four day holding time due to transportation delays or laboratory backlogs (CDFA, 2006). After transporting the samples to the warehouse, add 10 mL hexane to the bottle, replacing an equal amount of sample water. Add hexane under the fume hood and swirl bottle to mix the hexane and water.

3.1.6 Transport during sampling

Mark lids with appropriate analytical screen code. Rinse bottles with DI water, place bottles into an ice chest containing sufficient ice to keep the samples at 4°C for transportation. On multi-day trips, purchase additional bags of ice if needed to keep the samples at 4°C. For further information on sample transportation, packaging and shipping from field to the warehouse or laboratory, refer to DPR SOP QAQC004.01 (Jones, 1999).

3.1.7 Less common techniques for collecting grab samples

The below listed SW methods may not commonly be used, but may be needed in specific situations. Regardless of which of these less common methods are used, ensure to take samples from main areas of the stream, mindful not disturb sediment when placing equipment into the stream. DI can be used to clean and decontaminate between field sites, but more thorough cleaning is warranted between sampling trips.

3.1.7.1 Peristaltic pump

In very shallow waters, depth sampling, or for difficult to reach waters, SW staff may utilize peristaltic pumps to collect samples. Weighted strainers attached to tubing can collect water from various depths or reach difficult to access waters. For very shallow waters, a low-flow strainer allows sample collection. Peristaltic pumps can also be used for obtaining a vertical composite sample of a deeper water body. When using peristaltic pumps, follow sampling guidelines for autosamplers, including appropriate tubing and strainer cleaning, decontamination, and QC (Jones, 2000).

3.1.7.2 Bucket

A stainless steel bucket attached to a rope can be used to access difficult to reach waters, as from a bridge or pier. Caution needs to be taken to ensure bucket is secured to a stationary support (as bridge railing) and two people may be needed to retrieve a bucketful of water. Water must be of sufficient depth to ensure bed sediments are not disturbed. A bucket can also be used to collect water for taking water quality measurements.

3.1.7.3 Kemmerer sampler

Also when sampling from a pier or bridge, and in deeper waters, Kemmerer samplers may be utilized. Although not a common method, SW staff have access to several different sized samplers (1-L, 3-L, 4.2-L). Kemmerer samples can be quite heavy once filled with water, and may require two people to retrieve. Precaution should be taken prior to use by securing the sampler to a stationary object (as a bridge railing), wearing leather gloves, and decontaminating the sampler in the field with DI between uses. Refer to DPR video SOP Kemmerer Sampler for Surface Water or manual (Wildco, 2019) for details.

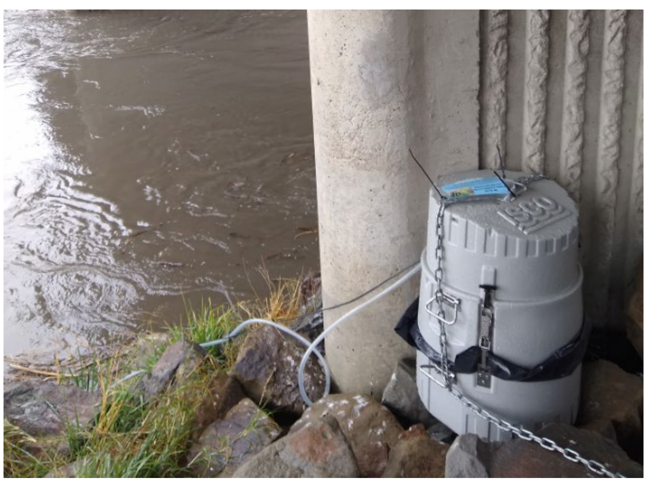


Figure 3: A Teledyne ISCO 6712 portable sampler secured in the field

3.2 Water Sample Collection with Autosampler

Composite samples are preferred when collecting storm water runoff. With the use of a portable sampler (Figure 3), collect either time-weighted or flow-weighted discrete or composite samples to fully characterize the complete storm runoff profile. When using portable samplers, additional preparation and planning is required to program, install/remove, and secure the samplers. For detail in using autosamplers, refer to DPR SOP EQWA005 (Jones, 2000).

3.3 Grab Sediment Sample Collection

Based on protocol objectives, collect sediment samples concurrently or independently of water monitoring. If collecting concurrently, always collect water samples first.

3.3.1 Site observation

Locate areas where fine-grained sediment is present on the bottom of waterbodies, generally in areas with low flow velocities or areas where obstructions have reduced flow. Select a mix of areas, i.e., right bank, left bank, stream center, areas of different depth, etc., to represent different depositional patterns.

3.3.2 Sample collection

Put on disposable gloves or long sleeved gloves; wear boots or waders depending on the conditions of sampling waterbodies.

Do not disturb the sediment sampling area with sampling equipment, water quality meters, or when wading in the stream. Approach sediment areas along stream bank if possible; if approaching the sampling area by wading, sample area from downstream.

Collect sediment from a depositional area by gently scraping the top 2-3 cm fine layer of the sediment with a trowel. Pour off overlying surface water. With a spatula, scrape off the loose sediment into a stainless steel container to create a composite sediment sample (Figure 4). See DPR Sediment Sampling Video for a visual demonstration.

Repeat from additional depositional areas until sufficient sediment has been collected and a mix of depositional areas has been sampled. Sample from at least four random sampling depositional areas.

3.3.3 Sample dispersal

Remove macrophytes, leaves, twigs, and pebbles in the composite sample. Thoroughly mix to homogenize the composite sample. Sandy sediment samples can be sieved with a 2 mm sieve in the field, especially if the composite sample is quite cluttered with debris. However, sieving samples with fine particles and high clay content in the field may be impractical. For further process in preparation of sediment samples for total organic carbon and chemical analyses, refer to DPR SOP METH008.00 (Lyon, 2009) and CDFA protocol EMON-SM-52-9 (CDFA, 2005).

Dispense the sediment into Mason glass jars (½ pint or pint). Generally, sediment is dispersed into three jars; for chemical analysis, organic carbon analysis, and a backup sample. Tightly cap the Mason jar.

3.3.4 Transport during sampling

Mark jar lid with identification, then place jar into a plastic bag. Store in an ice chest with sufficient ice to keep the sample at 4°C for transportation. For further information on sample transportation, packaging and shipping from field to the warehouse or laboratory, refer to DPR SOP QAQC004.01 (Jones 1999).

3.3.5 Long-term storage and cleaning

Upon arriving at the warehouse, pour off overlying water from the Mason jars to avoid breakage of the glass containers due to water expansion when frozen. Cap the Mason jars tightly, store in plastic bags, and freeze samples for future chemical and organic carbon analysis.

Clean the used equipment immediately after completion of each sampling site with tap/DI water in the field in order to avoid cross contamination between sites. When sampling is complete, more thorough cleaning and decontamination should be conducted at the laboratory, using Liquinox® (or similar), brush, tap water, and DI water.

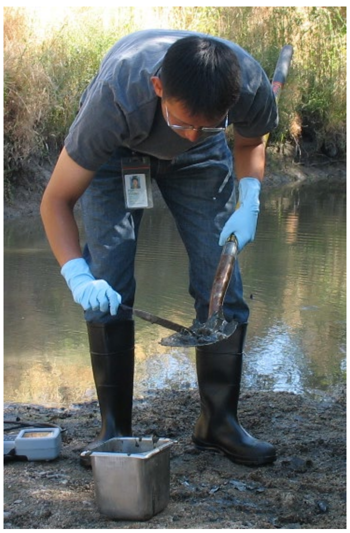


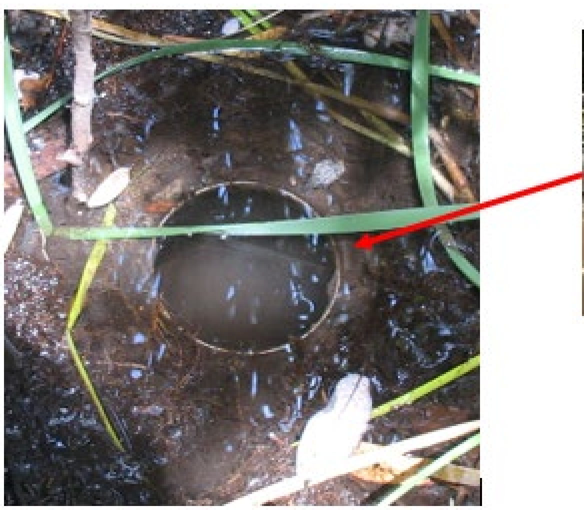
Figure 4: Collecting a grab sediment sample into a stainless steel container

3.4 Sediment Collection with Sediment Trap

Sediment can be collected with sediment traps, a passive method to collect sediments (Figure 5). With sediment traps, the time which the sediment accumulated is known, from trap installation to trap removal.

Place several containers below the stream bed in areas of low flow where suspended sediment can settle. Wide mouth quart Mason jars or 64 ounce Airscape® stainless steel containers make good sediment traps. Mason jars should be, and Airscape® containers can be, protected with concrete blocks or PVC tubing. Seal the space between the top of the sediment trap container and protectant with a wax like substance (e.g., toilet wax ring) for ease of removing (Budd et al., 2009). For safety, stainless steel containers are recommended over Mason jars.

When sampling, remove sediment traps and replace with cleaned and decontaminated containers. Cap, identify, and place container in a plastic bag, then store container in an ice chest with sufficient ice to keep the sample at 4°C for transportation. At the lab, pour off the overlying water, and sieve the sediment samples with a 2 mm sieve to remove macrophytes, leaves, twigs, and pebbles. After sieving, dispense sediment into smaller Mason jars (½ pint or pint) as described in grab sediment sample section, store in plastic bags, and freeze samples for future chemical and organic carbon analysis.



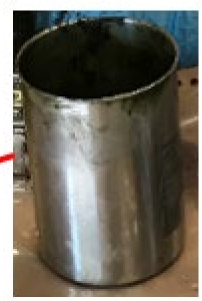


Figure 5: Stainless steel sediment trap installed in a stream bed

3.5 Sediment Collection with Polycarbonate cylinder

In streams with flowing waters, sediment can be collected via a polycarbonate cylinder (Figure 6). At the sampling site, insert polycarbonate tube into top 3 cm of sediment. Placed gloved hand or trowel under opening of cylinder at sediment end. Remove cylinder from the stream, then gently pour off overlying water, mindful not to disturb the sediment layer. Place sediment in stainless steel container for compositing. Repeat as necessary to obtain sufficient sediment. Sieve and thoroughly mix the composite samples, pour off overlying water upon arrival of the warehouse, and store as discussed above in the sediment grab section.

Figure 6: Sediment collected with polycarbonate tube

3.6 Water Quality

Record water quality measurements including ambient water temperature, specific conductivity, total dissolved solids, dissolved oxygen, salinity, and pH using a multi-parameter sonde or other water quality meter. Refer to DPR SOP EQWA012 (Edgerton, 2021). For a detailed manual on collecting water quality, refer to USGS water quality manual (USGS, 2018).

3.7 Flow

Flow can be obtained if samplings sites are at/near USGS gage stations (USGS Water Data) or other agencies flow meters. Alternatively, flow can be estimated with a hand held flow meter, fill bucket method, or floater method (Appropedia, 2021; Goehring, 2008).

3.8 Field QC

Field duplicate and/or field blank samples ensure data quality. A field duplicate sample taken concurrently with a field sample (e.g., two bottles at the end of the 2-bottle sampling pole) will give information on the precision of the analysis. A field blank sample indicate if there is artificially introduced contamination during field monitoring. SW programs will collect at least one field QC sample during each major sampling event (e.g., one field QC during the first flush rain event of the year), not to exceed 10% of the total samples collected for the monitoring year.

4.0 SAFETY

Safety is of utmost concern, and occurs in several forms, as preparation, driving, weather conditions, monitoring site conditions, etc. Prior to sampling, field staff should be well acquainted with DPR's Injury and Illness Prevention Program Field Health and Safety Program, which is available on Environmental Monitoring's internal web page. Listed below are other safety instruction for field sampling staff.

4.1 Pre-sampling preparation

4.1.1 Safety training

Surface Water staff are required to take the following safety trainings prior to participating in sampling. Most training is required on an annual or biennial basis. The project lead should ensure that all sampling staff are current with their training. Contact the department's training coordinator if training is needed.

4.1.1.1 Defensive driving training

4.1.1.2 CPR/First aid training

4.1.1.3 Heat illness prevention training
Power point presentation is available on Environmental Monitoring internal web page

4.1.2 First aid kit

All DPR vehicles are equipped with a first aid kit. Locate kits in vehicles used for travel and inspect to ensure the kit is stocked with appropriate first aid supplies.

4.1.3 Vehicle

When packing field equipment into vehicles, be mindful of shifting equipment during travel and pack to minimize equipment movement. Pack vehicle to increase the ease of access equipment at field sites, e.g., pack PPE in easy access, place ice chests to maximize ease of access.

Prior to traveling, inspect vehicle for safety issues, as low tire pressure, dirty windshield, headlights, mirrors, etc. Address issues as necessary.

4.2 **Safety when sampling**

4.2.1 Tailgate Safety Meeting

Prior to sampling, a tailgate safety meeting is held to alert the sampling crew to potential dangers. During adverse weather (hot, cold, rain, night monitoring), be mindful to adjust sampling accordingly. During hot weather, allowing sufficient shade and cooling areas (e.g., an air-conditioned vehicle). When sampling, be mindful of potential hazards as slipping and strong current. Never enter swiftly flowing waters.

4.2.2 Defensive driving

Practice defensive driving techniques during the trip. Observe speed limits and adjust speed and distance between vehicles based on traffic flow and weather/road conditions. For longer trips, rotate drivers and take rest breaks.

4.2.3 Parking

Park vehicles on safe and hard surfaces away from main traffic. If necessary to park on the shoulder along a roadway, engage emergency flashers and place traffic cones behind, alongside, and in front of the vehicle (Figure 7). Use traffic cones that are at least 18 inches tall. Place at least six traffic cones on the taper to alongside the roadway and vehicle, at a minimum of 100 feet from vehicle. Increase length of the buffer and number of cones with increasing road speed limits, up to 150 feet from the vehicle. For additional safety, also place traffic cones alongside and 50 feet downward of the parked vehicle. During night-time monitoring, use traffic cones with reflective bands or sleeves and a minimum of 28 inches tall cone. For more detail on traffic cone use, refer to the California Temporary Traffic Control Handbook, a manual developed by the California Inter-Utility Coordinating Committee (CATTCH, 2014).

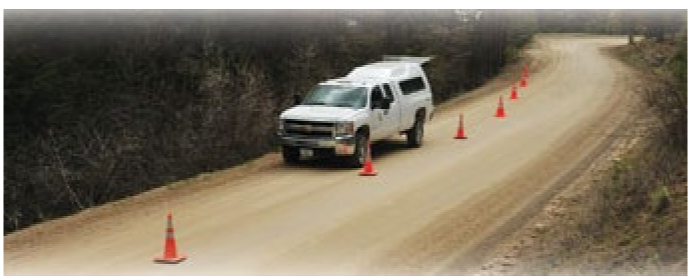


Figure 7: Traffic Cone Placement as pictured by the USS Forest Service. Surface water staff must only park in the shoulder area and never park to completely block a lane of traffic

4.2.4 Personal Protective Equipment

Wear personal protective equipment (PPE) appropriate for the weather and walking conditions. PPE includes gloves, reflective vests, boots, rain gear, and floatation vests. DPR's Injury and Illness Prevention Program Field Health and Safety Program gives information on appropriate PPE for sampling conditions.

5.0 REPORTING REQUIREMENTS

5.1. Complete field data sheets at each site to record site characteristics, water quality measurements, flow information, and bottle number for each analyte screen.

5.2. Complete COCs and sample check in sheets; refer to DPR SOP ADMN006 (Ganapathy, 2004).

5.3. When sampling is complete, notify lab liaison of analyte screen and number of samples collected.

5.4. Notify SW laboratory staff of any samples delivered for SW staff-conducted analysis (suspended sediment, organic carbon).

5.5. To archive, store field data sheets and COCs electronically on Surface Water's shared drive.

5.6. Enter field data and sample number/analyte screen into appropriate ACCESS database dependent on program (e.g., urban monitoring; agricultural monitoring).

5.7. At the end of the study, prepare the data for the project's annual report and submission of the data to the Surf Water Database coordinator (Ensminger, 2015).

6.0 STUDY-SPECIFIC DECISIONS

Refer to study protocol for study-specific decisions such as sampling site locations, sampling frequencies, data reporting and quality control, data analysis. Protocols can be found at the Environmental Monitoring Protocols web page.

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