Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for Sampling of Pesticides and Semivolatile Organics in Surface Waters

Version 3.1

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Date: August 20, 2015

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Date: December 19, 2011

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Date - February 8, 2012

EAP003

APPROVED: February 8, 2012
RECERTIFIED: August 20, 2015

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)
4/21/2010		Updated staff requirements, Updated cleaning procedures for US DH 79 and 81 nozzles and caps Updated bottle size/type Updated (added to) replicate MS/MSD sample collect method.	4.1, 4.11.1, 6.3.5 5.2; 6.5.2; 6.5.5 8.1.1	Debby Sargeant
12/19/2011	2.1	Updated definitions Updated carbamate bottle and preserv. Updated use of DH-81 Changed DH-76 sampler to DH-95 Changed procedure for DH-76 to DH-95 Changed reference for DH-76 to DH-95	3.9 5.3; 6.5.2; 6.5.5 5.9; 6.4.2 5.10- 5.10.7; 6.4.3 6.7-6.7.9 10.5	Paul D. Anderson
8/20/2015	3.1	Updated SOP to include semivolatile organics Updated purpose and scope Updated equipment to include supplies for large volume injection Added reference for decontamination SOP Clarified strategy for grab sampling	 1.1, 1.2 5.3 6.3,10.6 6.5.2,6.5.5	William O. Hobbs

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for collecting samples to monitor pesticides and semivolatile organics in surface waters.

1.2 Monitoring pesticides and semivolatile organics in surface waters can and often does cover a wide range of objectives. Some studies are designed to look for a few specific chemicals, and others are designed to look for a wide range of compounds. The term pesticide is used as a general term to group together many different use classes (herbicides, insecticides, and fungicides) of chemicals. The term semivolatile organics is a general term applied to organic compounds that have a boiling point higher than water and may vaporize at room temperature; they include: polycyclic aromatic hydrocarbons (PAHs), phthalates, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins and furans and phenols. For hydrophobic compounds, a relationship with Total Suspended Solids (TSS) may exist. This leads many monitoring projects to collect TSS samples alongside pesticide and organics samples.

2.0 Applicability

2.1 It is recommended that this procedure be followed by the Environmental Assessment Program when sampling surface waters to determine the presence and concentration of pesticides and semivolatile organics.

3.0 Definitions

3.1 Certificate of Analysis: Certificate provided by manufacturer ensuring bottles have been cleaned to EPA specifications.

3.2 EPA – Environmental Protection Agency

3.3 FISP – Federal Interagency Sedimentation Project

3.4 MSDS – Material Safety Data Sheet: These data sheets provide important information about a chemical's properties along with health and safety data. Other information about the chemical manufacturer, fire-fighting procedures, protective equipment requirements, and spill cleanup procedures are also provided.

3.5 MS/MSD – Matrix Spike/Matrix Spike Duplicate

3.6 MEL – Manchester Environmental Laboratory: Ecology laboratory that analyzes all pesticide samples.

3.7 TSS – Total Suspended Solids: A measure of the total amount of suspended material found in the water column.

3.8 US DH-81: depth integrating sampler designed by the USGS for use in wadeable rivers and streams between 1 and 4 feet.

3.9 US DH-95: depth integrating hand line sampler designed by the USGS for use in waters that are unsafe to wade but are not deeper than 15 feet and velocities not greater than 7.4 ft/sec.

3.10 US D-77: Teflon nozzle and cap for the US DH-81

3.11 USGS – United States Geological Survey

4.0 Personnel Qualifications/Responsibilities

4.1 Personnel collecting pesticide samples in surface waters should have prior experience conducting water sampling and should have a job classification equivalent to an Environmental Specialist 1 or higher.

5.0 Equipment, Reagents, and Supplies

5.1 1-liter manufacturer cleaned clear glass jars that are organic free with Teflon lid liners and a Certificate of Analysis

5.2 1000 milliliter manufacture cleaned amber glass jars that are organic free with Teflon lid liners and a Certificate of Analysis

5.3 l-gallon glass jar with Teflon lined cap and a Certificate of Analysis (only necessary for analysis by large volume injection).

5.4 20-milliliter manufacturer cleaned clear amber volatile organic analysis bottles that are organic free with Teflon lid liners and a Certificate of Analysis [preserved by Manchester Environmental Laboratory (MEL) with 0.05 milliliter of acetic acid]

5.5 Coolers and wet ice

5.6 Talc-free nitrile gloves

5.7 Sample tags

5.8 Chain of custody seals

5.9 TSS bottle (only necessary for studies collecting TSS samples)

5.10 US DH-81 (used in waters between 1 and 4 feet deep but still wadeable and that are not well mixed and have upstream water inputs) (Figure 1)

5.10.1 Wading rod handle and extension

5.10.2 Teflon US D-77 Caps pre-cleaned[1] to EPA specifications (EPA, 1990) and wrapped in aluminum foil with dull side in

5.10.3 Teflon US D-77 nozzles pre-cleaned to EPA specifications (EPA, 1990) and wrapped in aluminum foil with dull side in

5.10.4 US DH-81A adapter

5.10.5 1-liter glass bottles that will fit US D-77 nozzle pre-cleaned to EPA specifications (EPA, 1990) with opening covered by dull side of aluminum foil

5.11 US DH-95 (used in waters to deep or swift to safely wade but not deeper than 15 feet and velocities not greater than 7.4 ft/sec.) (Figure 2)

5.11.1 US DH-95

5.11.2 Hanger bar and pin used to attach sampler to rope or cable

5.11.3 A length of rope appropriate for the distance to be lowered to and into the water or a bridge crane with the appropriate length of cable

5.11.4 1-liter Teflon bottles with lids pre-cleaned to EPA specifications (EPA, 1990)

5.11.5 Teflon nozzle holder cap pre-cleaned to EPA specifications (EPA, 1990) and wrapped in aluminum foil with dull side in

5.11.6 Teflon nozzles (1/4" or 5/16") pre-cleaned to EPA specifications (EPA, 1990) and wrapped in aluminum foil with dull side in

5.11.7 O-ring retainer or rubber bands to secure the bottle in the sampler

5.12 Supplies Needed for Cleaning Sampling Equipment

5.12.1 Pesticide grade acetone and hexane – Acetone and hexane are not known to be carcinogenic or teratogenic. The MSDS for acetone can be found at http://www.sciencelab.com/msds.php?msdsId=9927062 and for hexane at http://www.sciencelab.com/msds.php?msdsId=9927187.

[1] The cleaning procedure for the sampling equipment that needs to be pre-cleaned is provided in Section 6.0.

5.12.2 Aluminum foil

5.12.3 Liquinox soap

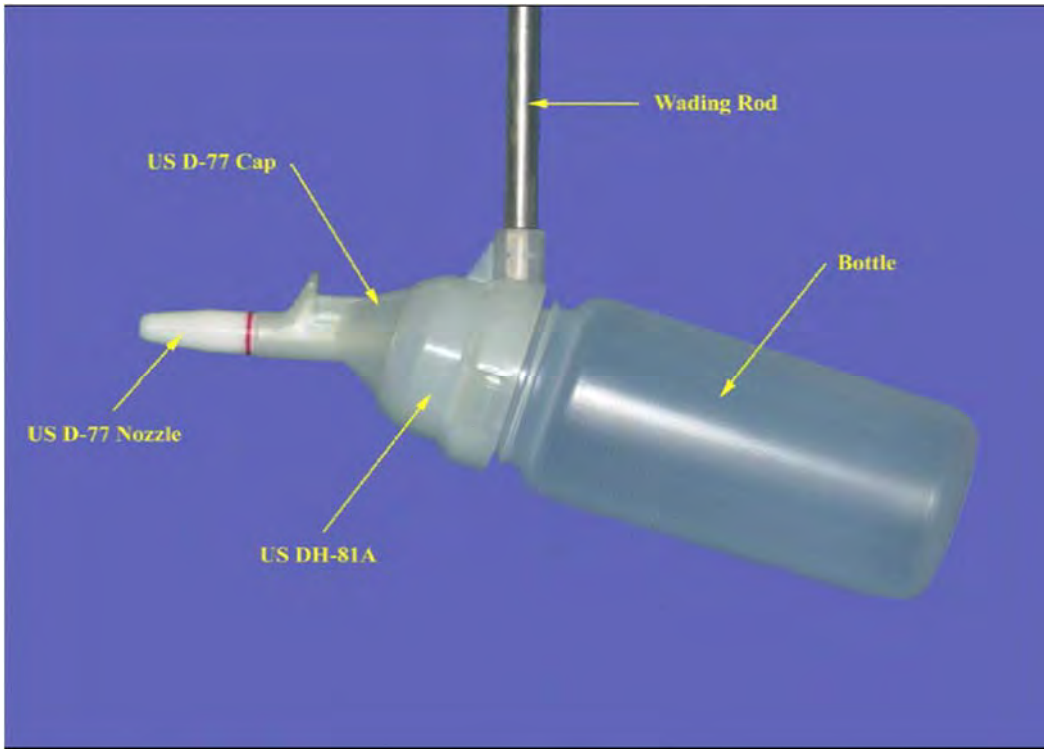

Figure 1. US DH-81 complete assembly.

Figure 2. US DH-95 complete assembly.

6.0 Summary of Procedure

6.1 General Sample Collection Techniques

6.1.1 Samples will be collected at quarter point transects unless the width of the river or stream makes doing so impractical or useless (i.e., > 1 ft depth). A quarter point transect consists of collecting water at 3 points on a line perpendicular to the stream. The points are generally near the right and left bank and near the center of the river or stream.

6.1.2 Always collect the sample facing upstream to avoid collecting what is re-suspended by wading. In slow-moving waters, movement upstream after each transect may be necessary to avoid the plume of re-suspended material.

6.1.3 Always wear nitrile gloves when sampling. The use of the nitrile gloves protects the sample from contamination from the hands of the sampler.

6.1.4 Take care not to bias the sample at any one depth of water. Contaminants may be distributed throughout the water column, and by taking a sample at one depth, the sampler may miss what is present elsewhere. Particular care should be taken to avoid collecting a disproportionate quantity of water or suspended sediment at the surface of the river or stream. Some pesticides and organics may partition to the surface layer or sorb to bedload constituents. Collecting water in a single region may bias the concentration in the sample.

6.1.5 When possible, keep the lid on the sample containers between transect points. This will avoid contamination from atmosphere and rain. This is not always possible and should be assessed on a case-by-case basis.

6.1.6 When possible, keep the sample containers out of the sun during sample collection. In addition, use amber bottles for those pesticides and organics susceptible to photolysis.

6.1.7 Fill sample containers to the shoulder. If testing for highly volatile products, sample containers should be filled to the top of container (no headspace). In this instance, volatile products are compounds with a Henry's Law constant greater than or equal to 10^{-3} atm*m^3/mole.

6.1.8 Take care not to disturb the substrate with the transfer bottle nor collect anything from the substrate.

6.2 Handling of Sampling Equipment and Bottles

6.2.1 No part of any piece of sampling equipment that will come into contact with the sample during collection should be touched without wearing nitrile gloves.

6.2.2 Never touch the inside of a sample container or Teflon lid liner even if wearing nitrile gloves.

6.3 Pre-Cleaning Procedure for US DH-81 and DH-76 parts and bottles, or other pieces of equipment that will come into contact with the sample water (Friese, 2014).

6.3.1 When cleaning sampling equipment follow all safety procedures and wear all necessary safety equipment as detailed in the Ecology Chemical Hygiene Plan.

6.3.2 Wash with hot tap water and brush with Liquinox detergent.

6.3.3 Rinse with tap water 3 times.

6.3.4 Rinse with deionized water 3 times, and let drain.

6.3.5 Rinse with pesticide grade acetone, and let dry in fume hood.

6.3.6 Rinse with pesticide grade hexane, and let dry in fume hood.

6.3.7 Wrap in aluminum foil with dull side towards sampling equipment.

6.4 Types of Sampling

6.4.1 Grab Sampling – Water collection method using a handheld 1 liter jar in waters less than or equal to 1 foot.

6.4.2 US DH-81 Depth Integrated Sampling – Water collection method using a 1 liter jar attached to a nozzle that is raised and lowered in the water column by a metal handle. This method is used in waters greater than 1 foot but less than 4 feet in depth, not well mixed, and have upstream water input.

6.4.3 US DH-95 Depth Integrated Hand Line Sampling – Water collection method using a 1-liter jar placed in the housing of a weighted sampling devices lowered by a rope or cable. The US DH-95 method is used in waters greater than or equal to 4 feet but not greater than 15 feet in depth and with maximum velocities of 7.4 ft/sec.

6.4.4 Automatic Sampling – water collection method where an automated mechanical sampling device is used to collect water over a period of time or a time specified by the user. This is a specialized type of sampling and will not be covered in this procedure manual.

6.5 Grab Sampling

6.5.1 The sampler fills out a field sheet with the date, time, samplers, station name, method of collection, sample number, and weather observations. At this time, the sampler will also fill out the sample label with all necessary information. This part of the procedure may be done in the office prior to sampling with the exception of the noting sample time and collection method.

6.5.2 The sampler will need 1000-milliliter amber bottles (to meet the number of analytes), 1 20-milliliter amber bottle, 1 1-liter transfer jar, 1 1-gallon jar if large volume injection will be used, and 1 1-liter polypropylene bottle (optional). Separate 1000-milliliter bottles will be used for the herbicide, current-use pesticide analysis except for carbamates, organochlorine pesticides, PCBs, PBDEs, dioxins and furans, and PAHs. The 20-milliliter bottle will be used for carbamate analysis. The 1-gallon jar is used for organochlorine pesticide analysis only if large-volume injection is being used as an analytical method. The 1-liter polypropylene bottle will be used for TSS.

6.5.3 The sampler will then take all of the containers and sample equipment to the sample site and put on nitrile gloves.

6.5.4 The sampler removes the lid from the transfer jar.

6.5.5 The sampler then uses the 1 liter transfer jar to collect water at each point of the transect. The 1000 milliliter amber bottles and 1-gallon jar will be filled by compositing 1/3 of the transfer bottle from each point of the transect. This equates to filling the jars 1/3 full at each point on the transect. The 20-milliliter bottle and the 1-liter polypropylene bottle will be filled 1/3 full from each transect point.

6.5.6 After each sample container has been filled, the sampler will place a sample tag with the date, time, study name, station name, laboratory sample number, and type of analysis

filled out. Take care to make sure the proper tags are placed on the correct sample containers.

6.5.7 Once the sample containers are labeled, the samples must be put in ice in a cooler. Placing the samples in a cooler in ice will bring down the temperature and preserve the samples before they are extracted and analyzed.

6.5.8 Upon return to the point of departure, the sampler will need to fill out a laboratory analysis required sheet and place chain of custody seals on the cooler(s). Laboratory analysis sheets and chain of custody seals may be found at the Operations Center or may be obtained from MEL.

6.6 Sampling Using the US DH-81 Depth-Integrating Sampler

6.6.1 The sampler will follow most of the directions listed above in the grab sampling section. What is described here pertains mainly to the set-up and use of the US DH-81 depth integrating sampler.

6.6.2 Before leaving the van, screw the DH-81A adaptor to the wading rod. All other parts of the US DH-81 should be left wrapped in foil until reaching the sample location.

6.6.3 Follow procedures 6.4.2-6.4.3. Sampling equipment for the US DH-81 are the US D-77 cap and nozzle, US DH-81A, and wading rod.

6.6.4 Remove the foil from the US D-77 nozzle and D-77 cap, and put them together. Place the single piece into the US DH-81A and turn the piece to lock it in place.

6.6.5 Remove the foil from the opening of the 1-liter pre-cleaned sample jar that fits the DH-81, and screw it into the UD D-77 cap. The US DH-81 is now fully assembled.

6.6.6 Fill the bottle at each transect point by moving the assembly up and down in the water column. The rate of movement up and down depends on the velocity of the water. If the water moves fast then the rate will be fast. If the water is slowly, then the rate will be slow. The rate of upward and downward movement determines how much water from each part of the water column enters the bottle. Rate of movement should be consistent in the vertical profile and between transect points at individual sample sites.

6.6.7 Once the bottle is full unscrew it and put the water into one of the sample containers. Repeat this process following procedure 6.5.5.

6.6.8 Complete sampling following procedures 6.5.6-6.5.8.

6.6.9 When sampling at the station is complete, remove the US D-77 cap and nozzle out of the US DH-81A and place it in a bag for cleaning. These pieces are expensive and should be re-used.

6.6.10 Further information on the use of the US DH-81 may be found in the Operator's Manual for the US-DH-81 Depth Integrating Suspended-Sediment Sampler, produced by the Federal Interagency Sedimentation Project (FISP).

6.7 Sampling Using the US DH-95

6.7.1 The sampler will use most of the procedures described in the grab sampling section. What is described here mainly pertains to the set-up and use of the US DH-95 sampler.

6.7.2 Follow procedures described in the Grab Sampling section (6.5.1-6.5.3). Sampling equipment for the US DH-95 is the sampler, cap and nozzle, 1-liter Teflon bottle, O-ring or rubber band, hanger and pin, and rope or bridge crane with cable.

6.7.3 Once at the sample site, remove the sampler from the box and attach the hanger using the pin. Tie the rope to the hanger using a secure knot, or attach the cable from the bridge crane. If possible, tie the bitter end of the rope, or secure the bridge crane to a solid object to prevent loss of the sampler.

6.7.4 Remove the nozzle and cap from the foil and screw the nozzle into the cap. Make sure that the nozzle is only finger tight. Remove the cap from the bottle, and screw the bottle onto the cap and nozzle. Place the entire set-up into the sampler, and secure it with an O-ring or rubber band.

6.7.5 Lower the sampler to the water at the first transect point. Lower the sampler into the water until the tail of the sampler just touches the bottom. Move the sampler up and down until the sampler is filled to 80% or 800 milliliters. Movement should be at a constant rate and the same at each transect point.

6.7.6 Raise the sampler; set it up on ground, making sure not to let the nozzle come into contact with any surface. If using a bridge crane, keep the sampler suspended. Remove the bottle, and fill each sample container 1/3 full. Repeat this process following procedure 6.5.5.

6.7.7 Complete sampling following procedures 6.5.6-6.5.8.

6.7.8 When sampling is complete, remove the cap and nozzle put them in a bag for cleaning and reuse. Parts are cleaned and reused because they are expensive. Remove the hanger and rope from the sampler, and put the sampler back in its box.

6.7.9 Further information on the use of the US DH-95 may be found in the Sampling with the US D-95TM Depth-Integrating Suspended-Sediment Sampler, produced by FISP.

7.0 Records Management

7.1 For each site where pesticides samples are collected, the following must be recorded in a field book:

7.1.1 Station name
7.1.2 Date and time of collection
7.1.3 Person or persons collecting samples
7.1.4 Weather observations
7.1.5 Method used for collection
7.1.6 Any field notes that may be pertinent to the investigation (e.g., dead fish)

7.2 All incoming MEL data should be stored in an organized manner for easy retrieval and review at a later date (e.g., File folders with the week number and date).

8.0 Quality Control and Quality Assurance Section

8.1 Field Quality Control Samples

8.1.1 Replicate Samples: Replicate samples consisting of two samples collected at the same time or in series should be included at the discretion of the project lead. Water for the replicate sample shall be collected at the same time as the regular sample at each point on the transect. These samples will estimate the total random variability (precision) of individual results.

8.1.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples: MS/MSD samples consisting of 2 extra volumes of water collected at one station should be included at the discretion of the project lead. These samples are used to evaluate the potential for significant bias in the results due to the interference of the water matrix.

8.1.3 Field Blanks (transfer blanks): A transfer blank is prepared by filling a sample container with pure water during routine sample collection to check for possible contamination from the surroundings. The transfer blank will also detect contamination from the containers or from cross-contamination during transportation and storage of the samples. Transfer blank samples should be included at the discretion of the project lead.

8.2 Results Quality Control

8.2.1 After MEL performs the sample analysis and obtains numerical results, the analyst and the lab QA/QC officer will review data and write up a case narrative. The results and narrative will be compiled into a report.

8.2.2 After laboratory review, the report will be given to the project lead or other designated project personnel. The person receiving the report will review the results and case narrative and look for any errors, omissions, or inconsistencies. It is the responsibility of the reviewer to investigate any issues and notify the project lead.

9.0 Safety

9.1 Field work done in connection with collecting pesticide samples in surface waters should follow the protocols described in the Environmental Assessment Program Safety Manual, paying special attention to those parts devoted to working in rivers and streams and working near traffic and from bridges.

10.0 References

10.1 Ecology. 2006. Environmental Assessment Program Safety Manual. Washington State Department of Ecology. Olympia, WA.

10.2 Ecology. 2006. Chemical Hygiene Plan & Hazardous Materials Management Plan. Washington State Department of Ecology. Olympia, WA.

10.3 EPA. 1990. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers. OSWER Directive #93240.0-05.

10.4 FISP. 2001. Operator's Manual for the US DH-81 Depth-Integrating Suspended-Sediment Sampler. http://water.usgs.gov/fisp/docs/Instructions_US_DH-81_010612.pdf

10.5 FISP. 2000. Sampling with the US D-95TM Depth-Integrating Suspended-Sediment Sampler. http://water.usgs.gov/fisp/docs/Instructions_US_D-95_000608.pdf

10.6 Friese, M. 2014. Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment. Washington State Department of Ecology, Olympia, WA. SOP Number EAP090. www.ecy.wa.gov/programs/eap/quality.html