

Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedure for Conducting Studies Using SPMDs.

Version 4.0

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Date -

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Date – 8/10/2016

EAP001

Original Approval Date: 2/7/2007

Most Recent Recertification Date: 8/10/2016

Internet 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	Summary of Changes	Sections	Reviser(s)
3/29/06	1.1	Revised section on PRC; editorial changes	6	Kirchmer/Kammin
3/30/06	1.1	Added language for Sections 4 and 7	4, 7	Johnson/Kammin
2/12/2007	2.0	Revisions based on Lake Chelan SPMD studies; editorial changes	all	Johnson/Kammin
11/30/2011	3.0	-Revised to incorporate recent experience and USGS guidance. -Expanded to be more comprehensive and user-friendly. -Includes Table of Contents to help staff use this lengthy document. -Includes interim procedures for data reduction and data management which will become a separate SOP.	all	Sandvik/Seiders
4/27/16	4.0	- revised to incorporate existing SOP for Data Reduction and Data Management - revised to incorporate contract lab ability to do dialysis - updated location of data repository and Appendix files	all	Hobbs

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Environmental Assessment Program

Standard Operating Procedure (SOP) for conducting studies using semi-permeable membrane devices (SPMDs) to monitor hydrophobic organic compounds in surface water.

1.0 Purpose and Scope

1.1 The scope of this SOP includes the following activities:

1.1.1 Planning the study.

1.1.2 Coordinating with different labs and field crews.

1.1.3 Scheduling and conducting the field work.

1.1.4 Shipping exposed SPMDs to lab for extraction.

1.1.5 Managing project information and data collected prior to lab analyses.

1.2 Section 10 includes abbreviated procedures for the reduction and management of SPMD data; procedures are more fully developed in a separate SOP for Data Reduction (EAP079; Seiders and Sandvik, 2013).

2.0 Applicability

2.1 This SOP is to be followed whenever Ecology studies use SPMDs. Careful planning and attention to detail are needed in all phases of using SPMDs in order for data to meet project objectives.

2.2 The use of SPMDs requires project leads to conduct a variety of QC procedures that have traditionally been performed within analytical labs. The extraction and analytical processes for SPMDs take place at two or three different laboratories which requires substantial coordination to ensure that adequate QC procedures are performed. Several QC procedures will help identify the sources and magnitudes of contamination within the sampling system so that these can be addressed during reduction of all sample and QC data.

2.3 *Description of SPMDs*

2.3.1 SPMDs are passive sampling devices used to concentrate a variety of hydrophobic organic chemicals from water (Appendix A). SPMDs were developed and patented by the U.S. Geological Survey. SPMDs are available in standardized design and are commercially available only through Environmental Sampling Technologies (EST), St. Joseph, MO. www.est-lab.com. The passive sampling is based on membrane- and lipid-water partitioning. SPMDs may sample any nonionic organic compound with a log K_{ow} value > 0 , but, in practice, a chemical's log K_{ow} should be greater than 2.5.

2.3.2 The capability of the SPMDs to concentrate organic contaminants is a major advantage over traditional water sampling techniques, since lower detection limits are achievable when the samples are analyzed. SPMDs are typically deployed for about 28 days and thus integrate temporal variability better than other short-term sampling techniques such as grab samples or 24-hour composite samples. SPMDs

concentrate the dissolved form of a contaminant, which is the form readily available to many forms of biota.

- 2.3.3 After contaminants are concentrated by SPMDs, the ambient dissolved concentrations of individual contaminants are estimated using ancillary data and models developed by USGS. The recoveries of Performance Reference Compounds (PRCs) spiked into SPMDs prior to deployment are used to correct for the effects of water velocity, turbulence, temperature, and biofouling on SPMD sampling rates. Total organic carbon data can be used to derive a whole-water chemical concentration from the dissolved data. More information about SPMDs can be found in Alvarez (2010) and Huckins, Petty, and Booij (2006).
- 2.3.4 While SPMDs don't have some of the problems encountered in sampling and comparing results from biota (e.g. age/size of the organism, trophic level, selective depuration of contaminants), results from SPMDs are sensitive to other factors that can compromise the quality and comparability of results. Such factors include: contamination from the sampling system, non-standardized field and lab techniques, use of different model inputs over space and time, use of different laboratories for low-level work.
- 2.3.5 The amount of a chemical absorbed by SPMDs is proportional to the local water concentration and the sampling rate of the SPMD membranes. Therefore, it may be difficult comparing relative levels of contaminants among sites using SPMD residues without having sampling rate information for each sample.

3.0 Definitions

- 3.1 Blank – A prepared sample, presumably free of the analytes of interest, used to assess possible contamination during various stages of the sampling and analytical process. A variety of field and lab blanks can be used with SPMDs to help define the sources and magnitudes of contamination.
- 3.2 Blank-correction – Results from blank samples can sometimes be used to adjust the final results of environmental samples. Blank correction typically involves subtracting the amount of known contamination (from the blanks) from the result for the environmental sample. Blank-correction techniques are allowed and described in some analytical methods. Other blank-correction techniques remain controversial.
- 3.3 Dialysis – The extraction procedure used for SPMD membranes. The dialysis process can be done by EST and a small number of analytical laboratories. It involves soaking the membranes in a bath of solvent to remove the organic compounds.
- 3.4 Dissolved-water concentration – The amount of target analyte estimated to be dissolved in the water where the SPMD was deployed. This value is determined using the USGS model.
- 3.5 Environmental Sampling Technologies (EST) – Exclusive commercial supplier of SPMDs (www.est-lab.com).

- 3.6 Extract – A solvent/solute mixture that contains the contaminants that were concentrated by the SPMD. The extract is the end product of the SPMD dialysis procedure used in the analysis.
- 3.7 Gas Chromatography/Mass Spectrometry (GC/MS) – Gas chromatography is a technique used to separate a complex mixture of organic materials into its components by heating the sample extract and carrying the mixture in an inert gas (mobile phase) through a column of absorbent material (stationary phase). A mass spectrometer is used to positively identify the compounds of interest by bombarding them with electrons to break them into characteristic fragments call ions and recording their masses.
- 3.8 Gel Permeation Chromatography (GPC) – A technique using packed columns to separate organic compounds based on molecular size.
- 3.9 K_{ow} – Octanol-water partitioning coefficient. This characteristic of any single analyte is one input used in the USGS model for estimating dissolved concentrations. K_{ow} values may be obtained from the scientific literature: note that multiple K_{ow} values may exist for any one analyte and that some analytes are very sensitive to the K_{ow} value used in the USGS model.
- 3.10 MEL – Manchester Environmental Laboratory.
- 3.11 MS – Matrix Spike. A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects.
- 3.12 PAH – Polycyclic aromatic hydrocarbons. A common group of organic contaminants having similar properties.
- 3.13 PBDE – Polybrominated di-phenyl ethers. A common group of organic contaminants having similar properties.
- 3.14 PCB – Polychlorinated bi-phenyls. A common group of organic contaminants having similar properties.
- 3.15 PO- Project Officer. The staff person responsible for designing, conducting, and reporting projects that involve environmental sampling.
- 3.16 Performance Reference Compounds (PRCs) - Analytically non-interfering compounds with moderate to relatively high fugacity (tendency to escape). PRCs are spiked into SPMDs prior to deployment.
- 3.17 QC – Quality Control. The routine application of measurement and statistical procedures to assess the accuracy of measurement data.
- 3.18 Residue – The amount of target analyte found in the SPMD extract. This value is one input variable for the USGS model which estimates a dissolved water concentration.

- 3.19 Sample – Defined as a specified number of SPMD membranes used together to sample any one site. A deployment typically uses 2-5 membranes.
- 3.20 Sampling Rate – The rate at which SPMDs take up analytes of interest. Sampling rates are affected by a multitude of variables and are typically non-linear. Sampling rates can be estimated using different techniques with the use of Performance Reference Compounds being favored.
- 3.21 Semipermeable membrane device (SPMD) – A passive sampler consisting of tubular, layflat, low-density polyethylene (LDPE) membrane containing a thin film of a high-molecular weight lipid (triolein). A standard SPMD consists of a 91 x 2.5 cm LDPE tube containing 1 mL of triolein (mass = 4.5 g, lipid volume = 0.001 L, membrane volume = 0.0037 L, SPMD volume = 0.0047 L).
- 3.22 SPMD shade device – a perforated aluminum cylinder that a canister with SPMD membranes can sit inside of to increase the percent shade for SPMD membranes. Additional shading maybe necessary for sunny, shallow water sites when sampling for light-degrading analytes such as polyaromatic hydrocarbons (PAHs).
- 3.23 Surrogate – A substance with properties similar to those of the target analyte(s) that are added to environmental samples for quality control purposes, to track extraction efficiency, and/or measure analyte recovery. Surrogates are unlikely to be native to environmental samples.
- 3.24 TidbiT™ - continuous temperature sampler and data logger. Used to monitor air and water temperature at SPMD deployment sites to help determine sample integrity.
- 3.25 Total Organic Carbon (TOC) – The amount of carbon found in organic compounds within a water sample.
- 3.26 Triolein – A high molecular weight lipid; the major nonpolar lipid found in aquatic organisms. A plant lipid is used in the SPMD.
- 3.27 TSU – Toxics Study Unit. A workgroup within Ecology’s Environmental Assessment Program.
- 3.28 USGS Model – A spreadsheet model that estimates the dissolved water concentration of analytes using SPMD residue and ancillary data. Written by David Alvarez, USGS, Columbia Environmental Research Centre, Missouri, USA.
- 3.29 Whole-water concentration – The amount of target analyte estimated to be the sum of the dissolved and particulate fractions in the water where the SPMD was deployed. This value can be estimated from a model that uses the dissolved water concentration and total organic carbon.

4.0 Personnel Qualifications/Responsibilities

- 4.1 Personnel leading projects that use SPMDs should have prior experience as project managers of studies involving organic contaminants and have a job classification

equivalent to an Environmental Specialist 3 or higher. The use of SPMDs is more complex than typical sampling techniques and requires skill in project management, organization, planning, coordination, and quality control. Project leads should also have experience and familiarity with analytical methods for organic analytes, particularly isotopic dilution methods for PCB congeners and dioxin/furans if these methods are used in the project.

- 4.2 Personnel conducting field work using SPMDs should have prior experience with varied water sampling techniques and be familiar with this SOP.

5.0 Equipment and Supplies

- 5.1 Equipment for sampling with SPMDs comes from various sources. The PO coordinates the gathering, preparation, and distribution of supplies and equipment to field crews.

- 5.2 General types of equipment and their sources are: SPMDs and carriers (EST). Deployment canisters, anchoring cables, and related deployment gear (EAP HQ and ROs). Spiking solutions and services (MEL, EST, and Contract Labs). Water sampling equipment such as bottles and kemmerers (MEL, EAP HQ). Typical field gear needs such as vehicles, boats, cleaning solutions, sample tags, coolers, personal field gear, and project file (EAP HQ and ROs). Examples of checklists for equipment needs are in Appendix B.

- 5.3 Other items for conducting SPMD projects includes tables and spreadsheets to help organize details about project management, coordination, communication, and actual treatment of samples (deployment and retrieval, field and QC samples, spikes, extracts, splits, and analyses). Section 7 discusses Records Management and includes an index of records needed for conducting SPMD studies.

Figures 1-3 show key components of SPMDs.



Figure 1. Single SPMD Membrane on a Spider Carrier.



Figure 2. SPMD Deployment Canister (five-membrane capacity).

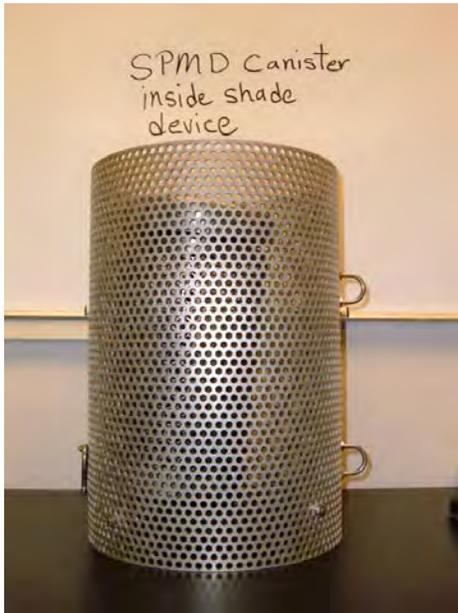


Figure 3. Shade Device for SPMD Canister.

6.0 Summary of Procedure

6.1 Project Planning

6.1.1 Successful SPMD sample collection efforts require planning at various levels. The QAPP will describe project goals and define the target analytes for locations to be sampled. Reconnaissance of the sample sites provides information needed to plan field efforts: legal permission may be required at some sites. Coordination involves clear communication and planning with staff from multiple laboratories as well as with field staff. Lab analyses and quality control, including spiking and extraction procedures must be exactly defined. Preparation for field deployment and sample collection must be carefully planned and executed. Finally, field efforts must be documented in order to obtain useable results from SPMDs.

6.1.2 Section 7 of this SOP (Records Management) describes the documents used for determining and communicating project needs to the varied parties involved in the SPMD project.

6.1.3 Sample and Lab Plan

6.1.3.1 Project planning is an iterative process beginning with general goals and ideas and then refining these to define specific objectives and needs at appropriate levels of detail. While developing the project QAPP, use the form “Master Sample and Analysis Plan” (see Section 7) to record the details for sampling and laboratory analyses. The QAPP will also describe the sample locations, target analytes, analytical methods, required reporting limits, sample contamination concerns, numbers of samples, the timing of samples, QA/QC plans, and timeframes to conduct tasks. Also use the form “Samples, Spikes, Splits, and Analyses Plan” (Section 7) to refine details about how each sample is treated with spikes, splits, and analyses. Other forms in Section 7 will be used for crafting your plans, communicating needs to others, and keeping track of information that will be needed for calculating final results from SPMDs.

6.1.4 Sample Site Reconnaissance

6.1.4.1 Obtain information about the site, access, local conditions, hydrology, site security, and any other information that will improve chances of a successful sample collection effort. Local knowledge can be very helpful determining a secure and usable location. While most reconnaissance can be done via phone, email, and office resources (e.g. Gazetteer, GIS, and other staff), an actual site visit is needed to determine equipment needs for deployment and other factors that may affect the sampling effort.

6.1.4.2 Review Ecology’s Policy 22-05 which addresses accessing private property. Determine the need for permits and/or permissions to collect samples at each site and contact the proper authorities. Application for permits may take several months or longer. Documented permission or proof of liability may be required from other

entities to gain access to the site. Liability insurance information can be obtained from the state through Ecology's Risk, Facilities, and Transportation Manager.

6.1.5 Laboratory Coordination

6.1.5.1 The Project Officer (PO) coordinates all laboratory efforts to ensure labs are providing the proper services at the proper times. This is a substantial role because multiple labs, staff, tasks, and timeframes are involved. The major entities involved in an SPMD project are:

6.1.5.1.1 Project Officer (PO): Defines analytical laboratory services that are needed and communicates such to all labs. Coordinates laboratory efforts according to needs and timeframes for the project. Works with MEL to develop RFQQ and RLS documents for contract lab services. Maintains documentation needed for coordinating project SPMD efforts and for obtaining useful results from SPMDs. Tracks shipping and billing of materials to ensure timeliness of services and payments.

6.1.5.1.2 Manchester Environmental Lab: The Organics Section Supervisor works with the PO on spiking solution needs, coordinates the preparation of spiking solutions, spike solution Standard Certificates, and coordinates MEL's analyses for many contaminants.

6.1.5.1.3 Manchester Environmental Lab: The Contracting Officer helps develop contracts with outside labs, including EST, for special services and analyses (e.g. HRMS for PCB congeners and dioxin/furans), validates contract lab results, and coordinates some shipping and receiving of sample extracts.

6.1.5.1.4 Environmental Science Technologies: Manufactures, prepares, and processes SPMDs for project; includes pre-field and pre-analyses spiking of PRCs, surrogates, extraction standards, and matrix spikes; conducts post-field cleaning, dialysis, and GPC cleanup of SPMDs, prepares and sends SPMD extracts to MEL. Works closely with the PO, MEL, and contract labs. Conducts some internal QC. It is worth checking with EST to determine what electronic file formats they can and cannot use.

6.1.5.1.5 Contract Lab: Performs analyses not done by MEL, such as dialysis of SPMD and HRMS for PCB congeners and dioxins/furans. Prepares and ships extraction and other standards to EST prior to manufacturing. Reports results to MEL and Project Lead who then validate and verify results.

6.1.5.2 Section 7 of this SOP (Records Management) describes the forms or records used for determining and communicating project needs to the varied parties involved in the SPMD project.

6.1.6 Spiking of SPMDs

- 6.1.6.1 The preparation of SPMDs includes spiking one or more membranes in each sample with various solutions to meet varied needs. This spiking may occur during manufacturing or after retrieval yet before dialysis, depending on the target analytes and the purpose of the spiking. Typical spiking solutions include PRCs, surrogates, and extraction standards. PRCs are typically added to the triolein prior to injection into the membranes. Other spiking may be needed depending on project goals. If a contract lab is necessary for analysis (e.g. HRMS for PCBs), the PO should work with the lab to determine the necessary concentration of *labelled* compounds used as PRCs.
- 6.1.6.2 Develop the spiking plan using the document “Samples, Spikes, Splits, and Analyses Plan” which is described in Section 7. The spiking plan is a critical tool for communicating the project needs to multiple staff at multiple labs. All parties involved with the project need to understand how all samples are created and handled. Lab errors or miscommunication about spiking procedures is not uncommon. Using incorrect spiking data in the data reduction process can affect project results by many factors (e.g. 2x to 50x). Be extremely careful in determining what spiking procedures are needed.
- 6.1.6.3 Appendix C shows the process which TSU and MEL’s Organic Chemistry Unit agreed to follow to meet spiking needs. Note that the PO is responsible for communicating and coordinating spiking and other project needs with the different labs involved in the project.
- 6.1.7 Extraction of SPMDs
- 6.1.7.1 The SPMD extraction procedure (referred to as dialysis) is carried out by a small number of laboratories. Some labs offer the option of GPC cleanup of the extracts. Some analytical methods (e.g. EPA 1668A for HRMS PCBs) have sufficient cleanup methods. Some of the SOPs for cleanup are on file at Y:\SHARED Files\SPMDs\SPMD Info. If a contract lab is required for analysis it is preferable that the lab have the capacity to do the dialysis also.
- 6.1.8 Splitting of Extracts
- 6.1.8.1 Extracts may be split by EST or other labs depending on the analyses requested. All cases where extracts are to be split need to be planned early in the project to ensure that labs have adequate sample to analyze, that desired reporting limits will be met, and that appropriate levels of spiked compounds are added in the correct sequence of events. All labs involved with the project need to understand the plans for splitting extracts so that spiking can be conducted properly and that results can be reported correctly. Again, the document “Samples, Spikes, Splits, and Analyses Plan” is the tool for communicating how samples are to be split.

6.1.9 Laboratory Analyses

6.1.9.1 The analytical methods that have commonly been used for SPMD studies are shown in Appendix D. Analysis of SPMD extracts is typically straightforward because the extract is a relatively clean matrix, consisting mostly of hexane. EST will ship the extracts to MEL or the contract lab will conduct the dialysis and analysis in-house.: shipping is described later in Section 6.4. Here are some issues to be aware of regarding analytical procedures:

6.1.9.1.1 Two methods have been used to quantify the PCB congener PRCs that are spiked into SPMDs: EPA 8081/8082 with ECD; and EPA 1668A using HRMS. Note that results from these two methods are not comparable: which must be considered if the project goal includes comparing study results to results from different studies. If EPA 1668A is used, ensure that ¹³C labelled compounds are used as PRCs which will not interfere with the analysis.

6.1.9.1.2 Some PCB congeners that are spiked into SPMDs may interfere with the analysis of some organochlorine pesticide analytes. Check with labs to ensure that spiking levels of Extraction Internal Standards, or other compounds used for QC will not affect the analyses for organochlorine pesticides.

6.1.9.1.3 Extracts may be split by factors of 2 or more in order for multiple analyses to be done on the same sample. This splitting of extracts may raise the detection and reporting limits for some analytes by factors of 2 or more such that desired reporting limits may not be achievable. Lab or field contamination may also raise reporting limits for some analytes.

6.1.9.1.4 Labs may have to adjust initial results to account for the number of splits performed. For example, if MEL analyzes an extract that has been split twice (which would be a 25% fraction of the original extract), the initial result will have to be multiplied by 4 in order to report the result as nanograms (ng) per sample. However, for isotopic dilution methods where the Extraction Internal Standards are added prior to extraction, no such multiplication is necessary because the method automatically corrects for such splits.

6.1.9.1.5 Be aware that MEL cannot provide Detection Limits (DLs) for results because MEL does not perform the extraction of the samples. Yet DLs and RLs (Reporting Limits) can be estimated using results from field blank samples as discussed in Section 8 on QC.

6.1.10 Quality Control

6.1.10.1 The sampling plan will include a substantial QC effort (30%-50% of samples according to Huckins, et al.). This larger-than-usual QC effort is needed because of the nature of SPMDs and finding analytes near the limits of detection, the use of multiple labs, and limited QC information available from EST. Appendix E describes the variety of QC samples that can be used in SPMD projects and Section 8 of this SOP further describes QC needs. Guidelines by USGS (Alvarez, 2010) also address QC practices. Some issues regarding QC are:

- 6.1.10.1.1 Expect significant contamination from various PCB congeners, PBDE congeners, and PAHs (from 20% to 150% of sample result values), especially in waters where ambient levels of contaminants may be low. Desired reporting limits for some of these analytes may not be achieved due to such contamination. Some sources of contamination have been identified and mitigated (e.g. lab sources such as solvent or surrogate solutions) yet other sources of contamination remain to be addressed. Suspected sources of contamination that may not be resolved soon include the PE tubing, lipid, and GPC process involved with the manufacture and processing of SPMDs.
- 6.1.10.1.2 Contamination of the sampling system may be addressed using two general approaches: results are censored based on the levels of contamination found in blanks, and results are corrected to account for the levels of contamination found in blanks. Blank-correcting SPMD results to account for lab and field contamination may be performed only if adequate QC data are collected (Section 8). The additional samples and analyses needed for blank-correcting other sample results will affect planning because of associated costs.
- 6.1.10.1.3 Scrutinize all information about spiking procedures to ensure the proper spiking information is given to those performing the spiking (e.g. EST and contract labs) and proper information is used in data reduction. Review what was requested, what labs report was done, and what analytical results show.
- 6.1.11 Documentation
 - 6.1.11.1 See Section 7 on Record Keeping for descriptions of critical documents to use and retain. A variety of documentation is essential for communicating and coordinating with the multiple labs and staff involved in SPMD projects. Much of the information in these documents is needed for later calculations and interpretations involving lab results from SPMD extracts. Templates or examples of records described in Section 7 are at Y:\SHARED Files\SPMDs\SOP Info\SOP v4 revision 2016.
- 6.1.12 Summary of Major Tasks and Timeframes
 - 6.1.12.1 Appendices F1 and F2 show major tasks in a timeline format. These appendices may be used as a checklist to help manage the project. Among the multitude of tasks involved in managing an SPMD project, the coordination and communication with MEL, EST, and Contract Labs requires a substantial effort to ensure SPMDs are prepared properly before and after deployment and before laboratory analyses. Appendix F1 addresses the major project tasks while Appendix F2 outlines the steps in selecting and working with Contract Labs.

6.2 *Prepare for Field Deployment*

6.2.1 Deployment Considerations

6.2.1.1 At each site, determine where and how to place the SPMD canister in the water column with the following considerations in mind:

6.2.1.1.1 Deploy SPMDs in a manner and location that is representative of the waterbody being sampled (e.g. avoid placing in stagnant water).

6.2.1.1.2 Locate samplers where they will be well hidden and yet can be found after deployment. Hiding can be more difficult if using a shade device because of the size. Consider using site replicates if a secure location cannot be found; only one needs to be analyzed. Take GPS readings, good field notes, and pictures to document the location of the sampler.

6.2.1.1.3 Allow for anticipated fluctuations in the water level during the deployment period. Water levels may change for various reasons, such as: flooding, spring runoff, irrigation withdrawals, and seasonal low-flow. Samplers should be placed where they will remain submerged. Retrieval cables attached to the samplers may need to be placed higher on the shoreline to allow retrieval at higher water levels.

6.2.1.1.4 If placing a sampler in a tidally influenced area, pre-determine the low and high tide levels during your sampling period to assure placing the sampler where it remains submerged.

6.2.1.1.5 Avoid strong currents which could damage or cause the loss of the device. High flow and turbulence can cause the sampler to tail and float (possibly away). Secure the sampler with multiple attachments.

6.2.1.1.6 A shade device may be needed to help prevent photodegradation of target analytes sequestered by SPMDs. The need for a shade device may influence the selection of the site and the deployment assembly.

6.2.2 Deployment Techniques

6.2.2.1 See the USGS document “Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies” by Alvarez (2010) for an overview of deployment techniques. The following techniques have been used successfully for EAP projects.

6.2.2.2 If the bottom of the waterbody is firm and not subject to siltation, the sampler can be laid directly on the streambed and cabled to the shore. If currents are strong, attach the sampler to a concrete block (Figure 4). If siltation is a concern, raise the sampler off the bottom with a concrete block or other object.



Figure 4. SPMD Sampler in Shade Device Attached to Concrete Block in Water.

Dams, docks, or other structures are convenient places to hang a sampler. Attach a weight if there may be currents strong enough to lift the canister (Figure 5).



Figure 5. SPMD Sampler Hung off a Dam.

6.2.2.3 A Bi-Pod Boom Assembly can be used to aid in deployment and retrieval if positioning the sampler at a stream bank is difficult. Instructions for its use can be found in Appendix G.

6.2.2.4 For deployments away from shoreline banks or structures, the sampler can be located at a desired depth between a surface buoy and anchor as in Figure 6. Be sure to consider the safety of swimmers, watersport participants, and vessels. Also consider the possibility of loss or damage to the sampler by vandalism, vessel traffic, and floating debris.

6.2.2.5 Follow these steps to deploy this subsurface assembly: Connect all parts of the assembly. Prepare the SPMD canister. Thread a slip-line through the eye of the snag anchor (do not tie this line to the snag anchor). Lower the main anchor (with SPMD and float) by the snag line to the bottom. Gently move the vessel and stretch out the snag line while lowering the snag anchor with the slip-line. Stretch out the snag line and snag anchor before releasing one end of the slip line. Retrieve the slip-line. Record the location of each anchor as accurately as possible using GPS. Retrieve

using a grappling hook dragged perpendicular to, and across the, snag line. A profiling depth sounder may be required to re-locate the snag line.

Water Surface

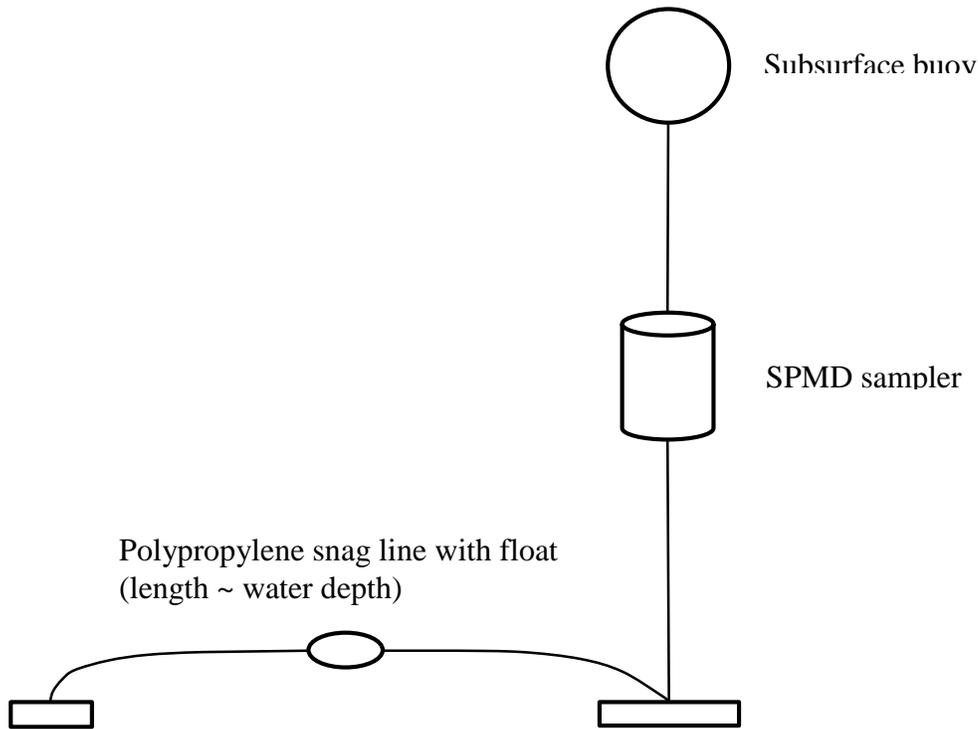


Figure 6. A Subsurface Deployment Method for SPMD Samplers.

6.2.3 Obtain Equipment

6.2.3.1 Careful planning and preparation of field equipment and supplies is essential for the smooth operation of deploying and retrieving the SPMD samplers. Reserving equipment from a common pooled resource must be made well in advance.

6.2.3.2 Reserve resources as needed: vehicles, boats, pooled and specialized equipment, freezer space, staging space for equipment, and staff.

6.2.3.3 Order any other sampling bottles from MEL (e.g. 60 mL poly bottles with acid for TOC samples, 1000 mL PE bottles for TSS samples).

6.2.3.4 Inventory all equipment and supplies needed for field efforts. Use an inventory and field checklists to guide your efforts.

6.2.4 Prepare Field Equipment

6.2.4.1 Clean and bag SPMD canisters and shade devices. Clean using either a pressure washer or hot liquinox soap scrub, then a clean-water rinse, then rinse with high-

purity acetone. Let dry before bagging together as an assembled unit to take out into the field. New plastic bags of appropriate size have been used successfully.

- 6.2.4.2 Stage all equipment in pre-reserved areas. Use a field checklist to help ensure all needed supplies are present.
- 6.2.4.3 Prepare TidbiTs™ for use per the continuous temperature monitoring SOP (Bilhimer et al., 2007). Launch TidbiTs™ using the parameters according to the project's plan (e.g. log temperature every 1 minute). Update the Java program on your computer before launching to assure proper operation of TidbiTs™. The latest versions of Java can be found at java.com. The HOBOWare software used for launching TidbiTs™ should automatically ask you to check for updates. Update HOBOWare as needed.
- 6.2.4.4 Calibrate other monitoring equipment and probes such as the Hanna DIST Probes for measuring conductivity and temperature.
- 6.2.4.5 Prepare Field Logs (Appendix H) and notebook for data entry using Rite-in-the-Rain paper. The Field Log is a two-page clipboard-style log which includes tasks and spaces for recording observations and measurements during deployment/retrieval of SPMDs.
- 6.2.4.6 Label and bag the SPMD sample cans. You can use a Microsoft Access program for printing on Avery address labels. The labels should be able to handle wet, cold, and hot environments or be protected from such. After applying labels, put the cans in a large Ziploc-type bag (~13"x18"x4mil) to help protect the SPMDs from dirt and moisture. Moisture tends to rust the cans and destroy the labels.
- 6.2.4.7 Transport SPMD membranes in cans using blue ice. Regular ice can be used if cans are placed in Ziploc-type bags to prevent rust formation. Placing the cans in bags also helps keep the cans dry and clean. Membranes are mounted on spider-carriers and shipped in argon filled one-gallon cans (argon is inert and heavier than air).
- 6.2.5 Prepare Field Folders
 - 6.2.5.1 Prepare a field folder for each sampling site so that field staff have everything they need for each site during deployment, midcheck, and retrieval. The field folders should contain the following items:
 - 6.2.5.1.1 Master list of sample information (e.g. sample IDs, site info).
 - 6.2.5.1.2 Sample tag labels for each site's samples, blank tags and labels, and extras.
 - 6.2.5.1.3 Field Log for each site, and extras.
 - 6.2.5.1.4 Field instrument manuals or instructions.
 - 6.2.5.1.5 Current SOP for SPMD planning and field deployment.
 - 6.2.5.1.6 Permits or written permission needed for access and sampling.
 - 6.2.5.1.7 List of contacts, field calendar, business cards.
 - 6.2.5.1.8 Field and float plans.
 - 6.2.5.1.9 Project QAPP.

6.3 *Deploy SPMDs*

6.3.1 Prepare Deployment Assembly

6.3.1.1 A variety of techniques can be used to attach canisters so they can be easily retrieved. Review the section on deployment techniques and determine what is needed for each site. Then prepare the deployment assembly before transferring the SPMDs to the water. The following is for a simple deployment using wire to attach the canister to an object on shore.

6.3.1.2 Attach a stainless steel wire or cable (1/8th diameter) to the canister keeping these points in mind:

6.3.1.2.1 Create a loop in the end of the cable which attaches to the canister. The loop is formed by swaging the terminal end of the wire to the standing part of the wire using aluminum or copper swages. Using a stainless steel thimble inside the loop protects the wire from chafing and may allow the wire to be used over and over again. The other end of the wire is commonly anchored to a dock, structure, or the bank (e.g. using rebar) to allow easy retrieval. The use of wire provides some security.

6.3.1.2.2 When SPMDs are used in marine or estuarine waters, use one or two copper swages when creating a loop in the cable. Do not use aluminum swages with the stainless steel wire because galvanic corrosion will consume the aluminum swage and result in loss of the canister with SPMDs.

6.3.1.2.3 Prepare cable by measuring and cutting appropriate lengths. Cable ends can be swaged directly to the canister and the object serving as the anchor; or prepare cable loops with thimbles to allow for quick attachment and release. Use stainless steel quicklinks for fastening to the thimble-protected loop of cable.

6.3.1.2.4 Do not mix copper and aluminum swages. Use only aluminum swages when using aluminum shade devices. Yet if using an aluminum shade device in estuarine/marine waters, use copper swages and attach a small zinc to the shade device to protect it from galvanic corrosion.

6.3.1.3 Secure an appropriate weight to the canister. Commonly used weights include concrete blocks (~10-20 lbs) and lead trolling weights (~8-16 lbs). Note that the weight of concrete in water is about 2/3 of its weight out of the water.

6.3.1.4 Attach a TidbiT™ using a zip tie on the top part of the canister for monitoring the water temperature. Attaching to the top should identify if the water drops below the top of the canister, or someone lifts the canister part way out of the water, not exposing the canister bottom. Record the TidbiT™ serial number in the field log.

6.3.1.5 Attach a TidbiT™ using a zip tie on a structure or tree near the sampling site for measuring air temperature. Try to locate the TidbiT in the shade. Ensure that the air monitoring TidbiT™ can be inserted inside a small PCV pipe with holes drilled in it

to shade the TidbiT™ from direct sun (Figure 7). Record the TidbiT™ serial number in the field log.



Figure 7. TidbiT™ Shaded in PCV Pipe.

6.3.2 Using a Shade Device

6.3.2.1 The top of the shade device is the opened end and the bottom is the end with the cross bar bracing. There is a hole for the cable to run through near the top and an oval slit for the bottom U-hoop of the canister to extend through for clipping.

6.3.2.2 Thread the cable through the top hole from the outside threading to the inside. Secure the membrane canister with the cable by attaching the cable that was threaded into the shade device to the canister's top U-hoop. By attaching the cable to the canister rather than the shade device, the canister with the membranes should remain in case everything else breaks away. The canister can also be pulled outside of the shade device in order to insert the membranes and secure the lid.

6.3.2.3 A weight, cement block, or other anchoring device can be attached to the bottom U-bolt of the shade device.

6.3.2.4 Make sure a TidbiT™ is attached to either the top of the canister or the top of the shade device. If the sampler will be lying on its side, make sure the TidbiT™ is attached where it will not be buried or damaged. Record the TidbiT™ serial number in the field log.

6.3.3 Insert Membranes into Canisters

6.3.3.1 Stop at this point and check all cable connections, anchors, tidbits, and other pieces of the array before proceeding. Check for potential sources of contamination at the deployment site.

- 6.3.3.2 Avoid or minimize contamination during actual deployment from sources such as: dirt and grease on hands, engine exhaust, wind-blown dust, smoke from nearby fires, and airborne smoke or clothing-entrained smoke from cigarettes.
- 6.3.3.3 Because SPMDs are potent air samplers, exposure to air during deployment and retrieval should be kept to a minimum by determining a plan of action among team members for quick and efficient execution of the steps listed below.
- 6.3.3.4 Set out the cans containing the SPMD membranes designated for the sample site. Note that the cans transporting SPMDs can have a maximum of 3 spider-mounted membranes. If using more than 3 membranes for the sample, make sure you have one can labeled 3 membranes and another can has the number of remaining membranes marked on it (e.g. for a 5-membrane sample, make sure 1 can is labeled as having 3 membranes and the other can is labeled as having 2 membranes).
- 6.3.3.5 Set out the other items needed for the deployment process such as the church key, spacers (if needed), zip ties, rubber mallet, carabineer, quick links, etc.
- 6.3.3.6 Wear talc-free nitrile gloves (SPMDs will sample natural skin oils as well as sunscreen and other possible contaminants).
- 6.3.3.7 Unscrew the lid on the deployment canister. Notice there is a threaded rod in the center of the device. The spider carriers will slide down this rod.
- 6.3.3.8 Loosen the lid of the can by prying the lid up with the church key (paint can opener) as shown in Figure 8. Note: screwdrivers, etc. will deform and damage the lid. The argon in the can is heavier than air yet it is unknown how quickly it dissipates once the can is open.



Figure 8. Loosening the Lid of the Can (church key in right hand, zip ties in left hand).

- 6.3.3.9 Start the stopwatch for timing the deployment process as soon as the lid is completely removed from the can.

- 6.3.3.10 Grasp the spider carrier by either the metal plate or center post and lift it out of the can taking care not to damage or abrade the membrane. Avoid touching the membranes. The width of the spider carrier is narrowest from one flat edge to the other flat edge. The flat edges must be oriented almost perpendicular to the inside edges of the can opening in order to pull the spider carriers out of the can or to put them back into the can (Figure 9).



Figure 9. Pulling a Spider Carrier with Membrane Out of the Can.

- 6.3.3.11 Slide the carrier onto the threaded rod in the canister (Figure 10). Make sure the threaded rod runs up through the carrier's center post (tube). A twisting (or small spin) motion sometimes helps the carrier slide down the rod.



Figure 10. SPMD Membranes in Canister.

- 6.3.3.12 Continue loading the other membranes (on spider-carriers) into the canister.
- 6.3.3.13 Add spacers if not enough membranes fill the canister.
- 6.3.3.14 Thread the lid back onto the canister. Start carefully to avoid cross-threading. Thread the lid down until the lid's outer rim covers the canister. Match the U-

shaped hoop on the lid with the U-shaped hoop on the canister body. Insert a zip tie through these hoops such that the lid cannot unscrew during the deployment.

- 6.3.3.15 If using a shade device, quickly slip the canister inside the shade device while taking up the cable slack by pulling the extra cable out the hole. Insert the canister's bottom U-hoop through the oval slit of the shade device and slide a carabineer through the U-hoop on the outside of the shade device.
- 6.3.3.16 Deploy the sampler in the water.
- 6.3.3.17 Stop the stopwatch when the membranes are underwater. In the field log, record the elapsed time those SPMDs were exposed to air and the time of day when the SPMDs went into the water.
- 6.3.3.18 Alternatively to minimize the amount of time the SPMDs are exposed to the air, steps 6.3.3.1 through 6.3.3.15 can be carried out underwater if it is safe to do so. The spider carriers are then loaded straight into the water. This should limit the exposure to under a minute.
- 6.3.3.19 Finish adjusting the position and securing the sampler once the membranes are in the water, but care must be taken to keep the membranes under water.
- 6.3.3.20 Carefully reseal the cans using a rubber mallet, ensure they are labeled with the site ID, and stow the cans in plastic zip bags.
- 6.3.3.21 Secure field Ecology Owner ID tags on anchor cable and then camouflage everything as much as possible.
- 6.3.3.22 Ensure all field information is properly recorded.

6.4 *Retrieval and Shipping*

6.4.1 Retrieval

- 6.4.1.1 A deployment period of approximately 28 days has generally afforded the best results. Consult with EST and/or the contract lab if a substantially longer or shorter deployment is desired.
- 6.4.1.2 The steps for retrieval are essentially the opposite of deployment. Set up equipment before pulling the sampler out of the water. Essential equipment includes nitrile gloves, cutting pliers, church key, cans for membranes, and a rubber mallet. Set out any other tools needed for retrieving the specific setup at each site.
- 6.4.1.3 Make sure the cans are labeled properly for the correct sampling site, date, sample number, and number of membranes in the can.
- 6.4.1.4 To minimized air exposure, determine a plan of action among the team members for the steps listed below that would be quick and efficient.

- 6.4.1.5 Wearing nitrile gloves and attending one sample at a time, loosen the lids of the cans before starting the stopwatch for timing air exposure during retrieval.
- 6.4.1.6 Note the time of day and start the timer when the SPMD membranes come out of the water.
- 6.4.1.7 Cut the zip ties on the canister/lid U-shaped hoops and unscrew the canister lid.
- 6.4.1.8 Remove the membranes from the canister and return them to the cans they were originally shipped in. When using more than 3 membranes, put number of membranes the can originally list: e.g. 2 membranes in the can labeled “2” and 3 membranes in the can labeled “3”.
- 6.4.1.9 Work quickly and avoid touching the membrane. The carrier needs to be inserted at a slight angle with the flat sides of the carrier sliding past the can opening.
- 6.4.1.10 Put the lids on the cans immediately.
- 6.4.1.11 Stop the stopwatch when the lids are placed on the cans. Make sure the cans are on a flat, hard surface and carefully reseal the cans immediately by tapping the lids down tight using a rubber mallet.
- 6.4.1.12 Document the time the SPMDs came out of the water and time that they were exposed to the air in the field log.
- 6.4.1.13 Retrieve the TidbiT™ on the sampler and the one placed nearby for monitoring air temperature. Re-record the TidbiT™ serial number in the field log.
- 6.4.1.14 Make sure the cans are labeled appropriately, put in plastic bags, and placed in coolers with ice as quickly as possible (blue-ice or bottled ice preferred over wet ice).
- 6.4.1.15 Ensure all field information is properly recorded.
- 6.4.1.16 Expose the Field Blank (if used at the site) according to methods described in Section 8.
- 6.4.1.17 Remove all anchoring system components including rebar stakes, lines, tags, etc.
- 6.4.1.18 Store sealed SPMDs in freezer as soon as possible upon return. The SPMDs should be shipped to EST as soon after retrieval as possible.
- 6.4.2 Shipping
- 6.4.2.1 Appendix I summarizes shipping instructions and responsibilities for SPMD membranes and spiking solutions. Ship materials by ground where indicated: do not ship by air because the composition of extracts may change due to pressure changes at altitude. Any reliable shipping company may be used.

- 6.4.2.2 Be sure to have EST notify the PO when SPMDs will arrive pre-deployment. Likewise, be sure to tell EST or the contract lab when to expect the SPMDs after retrieval from the field.
- 6.4.2.3 When shipping field samples to EST or the contract lab, include the LAR form which serves as the chain-of-custody form. All samples must be assigned sample ID numbers. Advise EST or the contract lab regarding any additional spiking required for the project (e.g. surrogates, extraction standards, and matrix spikes), if GPC clean-up of the extracts is desired, and if the extracts should be split to ship to different laboratories for analysis (see sample planning section).
- 6.4.2.4 Before EST or the contract lab processes the exposed SPMDs, review all TidbiT data to ensure the integrity of each SPMD sample. For SPMDs that were compromised in the field by exposure to air or other factors, determine whether to continue with processing and analyses of these samples. Samples that were compromised are likely to yield results that are unusable or of limited value. This is discussed in more detail in the Data Analysis section (Section 10).

7.0 **Records Management**

- 7.1 A variety of documents are used and maintained by the PO to organize and conduct a project using SPMDs. These documents or records communicate details to multiple labs and others involved in the project as well as provide all information needed to generate and support the reported results and their interpretation. The number of records in an SPMD project is often greater than those for typical projects because of the amount of QC and data processing involved with SPMD use. The PO maintains documentation relative to PO's part in the project while the laboratories maintain record relative to their role in the project.
- 7.2 Table 1 is an index of documents and records used in conducting SPMD studies. The first 23 items are related to project planning and the deployment/retrieval/shipment of SPMDs. Some of the first 23 items, and the remaining items in the table, are related to data reduction. All records involved in data reduction and data management are indicated in the 3rd column.
- 7.3 All records are needed for future use - which may be years or decades into the future. SPMD data are no longer stored in EIM so all records, results, and information used in a project are kept in an SPMD Data Repository on a shared drive. Table 2 shows the current and proposed structure of the SPMD Data Repository. The last column in Table 1 shows where each record belongs in the proposed repository structure.
- 7.4 Some of the records shown in Table 1 are described below. These records are presented generally in the order they are used in an SPMD project. The completion of records is self-explanatory in most cases: any questions should be directed to the authors of this SOP. These records are found in the appendices to this SOP located at Y:\SHARED Files\SPMDs\SOP Info\SOP v4 revision 2016\SOP Records and Locations Tbl 1 and 2 May 2016.xlsx. Examples for the last three items (quotes and agreements when hiring outside lab services) in this section are also found at Y:\SHARED Files\SPMDs\SOP\SOP Info\SOP v4 revision 2016.

Table 1. Index of Records for Conducting SPMD Projects. (can use as checklist for all phases of project)

orig order	Use for Plan + Deploy	Req'd for Data Redcn + Repostry	Record Description: Template in file or sheet format	SOP Apdx #	Code for location of records or templates	Repository folder where record goes for long-term storage
1	X		Types of Chemicals Sampled by SPMDs	A	a	
2	X		Field Checklist for SPMD Projects	B	a	
3	X		Process for Meeting Spiking Needs	C-1	a	
4	X		Spiking Solution Worksheet	C-2	a	
5	X		Analytical Methods for SPMD Projects	D	a	
6	X		Types and Characteristics of Quality Control Samples	E	a	
7	X		Major Tasks and Timeline for SPMD Projects	F-1	a	
8	X		Contract Lab Process and Timeline	F-2	a	
9	X		Bi-Pod Boom Assembly	G (in doc)	b	
10	X	X	Field Log for SPMD Projects	H	a	Field Data
11	X		Shipping Instructions and Responsibilities	I	a	
12	X	X	Master Sample and Analysis Plan	J	a	Planning Documents
13	X	X	Samples, Spikes, Splits, and Analyses Plan	K	a	Planning Documents
14	X	X	Spike Solution Standard Certificate from MEL	L	a	Planning Documents
15	X	X	Draft Spiking Instructions from MEL	M	a	Planning Documents
16	X	X	EST Services Summary	N	a	Planning Documents
17	X	X	Request for Quote - for EST	Other	c	Planning Documents
18	X	X	Request for Qualifications and Quote - for Contract Labs	Other	c	Planning Documents
19	X	X	Request for Laboratory Analyses - for Contract Labs	Other	c	Planning Documents
20	X	X	Project QAPP	Other	d	Planning Documents
21	X	X	Lab Analysis Required (LAR) Form	Other	e	Planning Documents
22	X	X	Index of Records for Conducting SPMD Projects	Table 1 (in doc)	j	Project General Info
23	X	X	Structure of Repository for SPMD Study Data	Table 1 (in doc)	j	
24		X	Deployment time and temperature	RR-1.123 *	f	Field Data
25		X	Deployment time, temp, flow	RR-1.45 *	f	Field Data
26		X	SPMD Air Exposure Times	RR-2	f	Field Data
27		X	Field & Membrane Notes	RR-3	f	Field Data
28		X	Ancillary data (e.g. TOC, TSS, flow)	RR-4	f	Lab Results
29		X	PRC Recoveries	RR-5	f	Lab Results
30		X	SPMD residue results, EDD format; includes CL work	RR-6	f	Lab Results
31		X	Log Kow's Used in USGS Model.	RR-7	f	Data Reduction & Modeling
32		X	USGS model used for estimations	RR-8	f	Data Reduction & Modeling
33		X	Water Concentration Estimates (Dissolved, Whole)	RR-9	f	Data Reduction & Modeling
34		X	Field Replicate data	RR-10	f	Lab Results
35		X	Sample site description	RR-11	f	Project General Info
36		X	Project Summary Form	RR-12	f	Project General Info
37		X	EST Membrane Condition Sheets	RR-13	h	Case Narratives
38		X	Data reduction process/checklist	RR-14	f	Data Reduction & Modeling
39		X	Checklist for Reviewing Contract Lab Data Packages	RR-15	f	Lab Results
40		X	MEL Case Narratives, for CL too; includes hardcopy results	Other	g	Case Narratives
41		X	Project Final Report	Other	d	Project General Info
42		X	Any other information pertaining to the study	Other	i	in appropriate folder

Notes:

* - Some of these formats could be simplified and/or combined

Codes for Location of Record or Templates

a	Y:\SHARED Files\SPMD\SOP Info\SOP Plan & Deploy templates Sep 2011.xlsx
b	Y:\SHARED Files\SPMD\SOP Info\Apdx G - Bipod Boom Assy.docx
c	Y:\SHARED Files\SPMD\SOP Info\RFQ,RFQQ,RLA example.docx
d	PO: Word doc, filename may vary
e	PO: Excel table or MEL hardcopy, filename may vary
f	Y:\SHARED Files\SPMD\SOP Info\SOP Data Redcn & Repository templates Sep 2011.xlsx
g	PO file: PDF files from MEL
h	PO file: scan EST documents
i	PO file: other
j	Y:\SHARED Files\SPMD\SOP Info\SOP Records & Locations Sep 2011.xlsx

Table 2. Structure of Repository for SPMD Study Data.							version: 8/29/12
Folder Level 1	Folder Level 2	File Level	File Type	Auditor: present, absence (P/A)	Auditor Note	Auditor: Completion Date	
* Project Name							
* 1_Project General Info							
		RR-11 Sample site descriptions	xlsx				
		RR-12 Project summary	xlsx				
		Other: Report	pdf, docx				
* 2_Planning Documents							
		Other: Project QAPP (+addendums)	pdf, docx				
		J. Master Sample+Analysis Plan	xlsx				
		K. Table of Sample-Spike-Split-Analyses	xlsx				
		L. Spike Solution Standard Certificate	pdf				
		M. Draft Spiking Instructions from MEL	pdf				
		N. EST Services Summary	xlsx				
		Other: Request for Quote - for EST	pdf, docx				
		Other: Request for Qualifications and Quote - for Contract Labs	pdf, docx				
		Other: Request for Laboratory Analyses - for Contract Labs	pdf, docx				
		Other: Lab Analysis Required (LAR) Form	pdf, xlsx				
* 3_Field Data							
		H. Field Logs	pdf				
		RR-1.1 TidbiT instructions	xlsx				
		RR-1.2 Deployment Temperature	xlsx				
		RR-1.3 Deployment Time	xlsx				
		RR-1.4 Streamflow	xlsx				
		RR-2 SPMD air exposure times	xlsx				
		Field & Membrane Notes (optional compilation of notes for effective cross referencing field issues, spiking, and other membrane handling issues)	xlsx				
* 4_Case Narratives							
		RR-13 Membrane Condition Sheets	pdf				
		Other: Case Narratives	pdf				
* 5_Lab Results							
		RR-3 Ancillary data	xlsx				
		RR-5 SPMD Residue and Ancillary Results (original EDD format)	xlsx				
		RR-15 PCB congener data review	pdf, xlsx				
*6_Data Reduction and Modeling							
		RR-4 PRC recovery	xlsx				
		RR-6 SPMD Residues-compiled	xlsx				
		RR-7 Log Kow's	xlsx				
		RR-8 USGS model used	xlsx				
		RR-9 Water Concentration Estimates	xlsx				
		RR-10 Field Replicate evaluation	xlsx				
		RR-14 Data reduction steps	xlsx				
		RR-16 Total Water Concentration Estimates	xlsx				
*7_Audit Report							
		Table 1. Auditor's Index of Records	pdf, xlsx				
		Table 2. Auditor's Copy of Repository Structure	pdf, xlsx				
		Copy of PO RR-14 Data Reduction Tasks for SPMD Data	pdf, xlsx				
		Other: Auditor's Report and Recommendations	pdf, docx				
Notes:							
* All folder names begin with the "Project Year_Project Name" (e.g. 2007-08_Potholes)							
Repository for SPMD data is located at EAP Sharepoint site.							

- 7.5 Master Sample and Analysis Plan
 - 7.5.1 This spreadsheet (Appendix J) is the master plan for showing site, sample, spiking, and analytical characteristics for the project. The spreadsheet also serves to:
 - 7.5.1.1 Identify the lab analysis planned for each sample.
 - 7.5.1.2 Identify QC requirements, especially spiking needs.
 - 7.5.1.3 Document lab and field identification codes.
 - 7.5.1.4 Serve as a basis for other records and spreadsheets used in the project.
 - 7.5.1.5 Determine costs for materials and analytical services.
 - 7.5.2 The structure of the spreadsheet should be adjusted to suit the project, especially when other analyses or spiking plans are used. All fields in the example are required for all projects because of recent efforts for TSU to be consistent in communications with MEL, EST, other labs, and for long-term data management in the SPMD Data Repository.
- 7.6 Samples, Spikes, Splits, and Analyses Plan
 - 7.6.1 The Appendix J spreadsheet is a refinement of the Master Sample and Analysis Plan to show exactly how each sample is to be spiked, extracted, split, and analyzed. This table is the result of an iterative process that includes reviews of drafts for spiking solutions, spiking instructions, and spiking plans by all parties involved until a common understanding is reached by all. SPMD projects typically involve multiple labs and staff: a combination that can result in differences in language, definitions, and understanding of SPMDs. Good coordination is needed in executing this and other parts of the project.
 - 7.6.2 A draft of the Sample, Spikes, Splits, and Analyses Plan table is developed by the PO who then coordinates its review and comment by all labs involved in the project (MEL, EST, and the Contract Lab). Labs may require or suggest changes to the spiking or splitting phases based on the nature of target analytes, analytical methods, or the volumes and concentrations of spiking solutions. The summary is then finalized after all parties involved reach agreement on the plan. Before any spiking is actually performed, the PO must give written permission to EST to conduct the spiking.
- 7.7 Spike Solution Standard Certificate from MEL
 - 7.7.1 This record (Appendix L) identifies and shows the contents of spike solutions created by MEL. Spike solutions are considered “standards” and each standard has a unique identifying code. The certificate shows the solution’s analytes with their respective CAS numbers, concentrations, and units of measure. Also given are relevant data such as: descriptive name, type of standard, the solvent used, the dates of preparation and expiration, the volume, the name of the preparer, and storage instructions. The certificate is also “certified” by the preparer and a reviewer. The Standard Certificate is generated through MEL’s LIMS system and should accompany any shipment of spiking solutions. These certificates do not include

spiking instructions for SPMDs: spiking instructions are given in a separate record because of differences across projects.

- 7.7.2 Other labs such as EST and contract labs will also provide documentation of the contents of the spiking solutions they create. These may or may not be certified, yet should still accompany any solutions that are shipped. During the project planning process, the PO will get copies of all spiking solutions to be used and review them to ensure that the solutions and associated instructions are appropriate for each act of spiking.
- 7.7.3 When using a contract lab for high-resolution GC/MS analysis ensure that labelled compounds are used if possible. These compounds may not be available if they are being used as matrix spikes. Labelled compounds ensure the congeners or compounds will not be found naturally.
- 7.8 Draft Spiking Instructions from MEL
- 7.8.1 MEL creates this table (Appendix M) which shows sample information and spiking instructions for spiking solutions prepared by MEL. The PO reviews MEL's instructions and then uses the information to populate the record above called "Summary of Samples, Spikes, Splits, and Analyses". The PO may need to discuss the content of spiking solutions and the spiking instructions with MEL to ensure common understanding about the nature of samples, spiking, splits, and analyses.
- 7.9 EST Services Summary
- 7.9.1 This spreadsheet (Appendix N) is derived from the Sample Analysis Plan (above) and is used to communicate exactly what materials and services are needed from EST. The EST Services Summary is included as part of the Request for Quote document (described below). Depending on the timing of the planning process, the final record called Summary of Samples, Spikes, Splits, and Analyses may or may not be part of the EST Services Summary.
- 7.10 Request for Quote – for EST
- 7.10.1 A formal document that specifies the materials, services, and timeframes needed from EST for the project. This document (referred to as an RFQ) is drafted by the PO with input from the MEL Contract Officer. The PO must be very clear and complete in what services EST is to provide. EST is the sole-source provider of services related to the manufacture of SPMD membranes – so we don't need to go through the competitive bidding process. The RFQ's Statement of Work must include:
 - 7.10.1.1 The agreement between Ecology and EST.
 - 7.10.1.2 Project description and timeframes.
 - 7.10.1.3 EST Services Summary (a table)
 - 7.10.1.4 The Summary of Samples, Spikes, Splits, and Analyses (a table)
 - 7.10.1.5 Extraction and cleanup (if necessary).

- 7.10.1.6 Internal QC.
- 7.10.1.7 Description of documentation that EST is to provide.
- 7.10.1.8 Shipping instructions.
- 7.10.1.8 Contact information for Ecology staff with whom EST may need to work with.

- 7.10.2 When completed, MEL's Contract Officer sends the document to EST who replies with a price quote for the work described. After the quote is received and any questions resolved, EST is informed that the project will proceed and the RFQ becomes the record of services that EST is to provide. The development and processing of an RFQ must follow agency guidelines which MEL's Contract Officer usually handles. Depending on the timing of the planning process, the final Summary of Samples, Spikes, Splits, and Analyses may or may not be part of the EST Services Summary. An example of an RFQ is located at Y:\SHARED Files\SPMD\SOP Info\SOP v4 revision 2016.

- 7.11 Request for Qualifications and Quote - for Contract Labs

- 7.11.1 A formal document similar to the RFQ described above, yet the RFQQ is used when we must have some work go through the competitive bidding process. The development and processing of an RFQQ must follow agency guidelines which MEL's Contract Officer usually handles. This document is drafted by the PO with input from the MEL Contract Officer. Again, the PO must be very clear, specific, and complete in describing the needed services. The RFQQ's Statement of Work must include:
 - 7.11.1.1 The nature of the agreement between Ecology and the successful bidder.
 - 7.11.1.2 Summary and timeframe of needs for the project.
 - 7.11.1.3 Items for analytical services, including preparation of spiking solutions.
 - 7.11.1.4 Reporting of results, including limits on blank contamination and data formats.
 - 7.11.1.5 Standard operating procedures for dialysis of the SPMD
 - 7.11.1.6 Contact information for MEL Contract Officer and SPMD Project Officer.

- 7.11.2 Many of the items above can be summarized in tables, such as the numbers of samples for analysis and their timeframes, data reporting formats, and specifics on the congeners to be used for various spiking operations. When complete, MEL's Contract Officer sends the document out to bid. Interested labs then provide a response package which includes a price quote for the work described. MEL's Contract Officer reviews the bid response and may recommend a lab to the PO. Once a lab is selected, the PO and MEL can begin to work out further details about the project. Prior to the Contract Lab receiving extracts for analysis, MEL's Contracting Officer will prepare another document described below: the Request for Laboratory Services. An example of an RFQQ is located at Y:\SHARED Files\SPMD\SOP Info\SOP v4 revision 2016.

- 7.12 Request for Lab Services - for Contract Labs
- 7.12.1 The Request for Lab Services (RLS) is similar in content to the RFQQ described above yet it contains the finalized sample plan and instructions for the contract lab. MEL's Contract Officer develops the RLS and the PO must review it before the RLS is sent to the contract lab along with the SPMD extracts. The RLS contains the Scope of Work (SOW) used in the RFQQ and this SOW may have some minor modifications based on the actual numbers of samples to be analyzed. The RLS will also contain the spreadsheet "Summary of Samples, Spikes, Splits, and Analyses". An example of an RLS is located at Y:\SHARED Files\SPMD\SOP Info\SOP v4 revision 2016.
- 7.13 Field Logs
- 7.13.1 The Field Log (Appendix H) is the form to record data and check off tasks performed during field activities such as deployment, mid-check, and retrieval. All items in the Field Log must be filled in by field crews except those marked as "optional". Some items provide information needed to process data in case there are failures in QC or other processes.
- 7.14 Laboratory Forms Used by MEL
- 7.14.1 See Ecology's "Lab User's Manual" for further description and use of these forms:
 - 7.14.1.1 Pre-Sampling Notification (PSN) form: This form is used to give MEL a brief accounting of plans for sampling and analysis, including the where, what, and when you are planning to collect and submit samples.
 - 7.14.1.2 Laboratory Analyses Required (LAR) form: This is the paperwork that must accompany all samples when they arrive at the laboratory. This form is to be filled out in triplicate. Request these forms from MEL's Sample Coordinator or use an Excel-based template which can easily be photocopied or sent electronically. This form also serves as the Chain of Custody form that accompanies SPMD samples and sample extracts during shipping among labs. The labs receiving samples or extracts need to be instructed to fill out the Chain of Custody portion of the form and return it to MEL with the extracts and/or results package. Work with EST or the contract lab to ensure they properly fill out the form and add any other information needed about the samples, such as the temperature of the container holding the SPMD cans shipped to EST. It is likely that a contract will also have their own Chain-of-Custody form that accompanies the samples during submission; MEL should receive a copy of this form in addition to samples being logged on the MEL LAR.
 - 7.14.1.3 Sample Container Request form: This form is used to order sample containers needed for your sampling event(s), and is usually submitted along with the Pre-Sampling Notification form.
- 7.15 Other Records

- 7.15.1 There will likely be other documents to manage, such as:
 - 7.15.1.1 Permission to access sampling sites.
 - 7.15.1.2 Lists of contacts information related to the project.
 - 7.15.1.3 Maps, images, graphics as needed, for example: to locate sites or show deployment assembly.
- 7.15.2 Additional records needed for data reduction and management are described in Section 10 - Data Management and Data Reduction: Interim Procedures.

8.0 Quality Control and Quality Assurance Section.

- 8.1 Quality control and quality assurance practices are described for three general locations: the analytical laboratories, the field, and at EST.
 - 8.1.1 Field quality control consists of following procedures for handling SPMDs, ensuring sample integrity (security, submergence, and sometimes shade), and use of replicate and field blank samples. The use of field blanks is addressed more fully below than other blanks because it has been the most important blank in characterizing contamination.
 - 8.1.2 EST handles or creates a variety of QC samples because most tasks involving SPMDs occur at EST. These tasks include the: manufacture, storage, preparation, pre- and post-field spiking, extraction (dialysis), GPC cleanup, splitting of extracts, and ampulizing the extracts for transport. USGS (Huckins, et al., 2006; Alvarez, 2010) describe the need for, and types of, various QC samples. All of these QC samples aim to characterize contamination at various stages in the processing of SPMDs. The types of QC samples used by Ecology and aspects of the SPMD process they represent are shown in Appendix E. Some QC samples are shown as required while others are optional. Past studies have used various QC samples to better characterize sources and magnitude of contamination in the SPMD process. Some QC samples are provided by EST at little or no cost.
 - 8.1.3 The analytical laboratories include MEL and contract labs. MEL handles analyses for various pesticides, PBDEs, and PAHs. Contract labs handle analyses for HRMS methods for PCB congeners and dioxins/furans. Laboratories use a variety of method-specific internal QC practices to evaluate the performance of their analytical systems. Descriptions for most of these practices are beyond the scope of this SOP, yet some are discussed because they are specific to SPMDs.
- 8.2 Multiple laboratories are involved in SPMD projects resulting in a variety of QC procedures being employed at different locations. Some of these procedures may need to be coordinated among the labs, such as ensuring that the mass of certain analytes spiked into SPMDs for one QC purpose do not interfere with the analysis of the same or different target analytes. The Project Officer is the lead person to ensure that needed coordination among laboratories happens in a timely manner.

- 8.3 *Field Quality Control*
- 8.3.1 Procedures for handling SPMDs in the field, assuring security, and providing shade are addressed elsewhere in this SOP. Procedures for ensuring submergence of SPMDs are partially addressed in the deployment and field logs while the practice for ensuring submergence uses TidbiTs as described below. The use of field replicate samples and field blanks are also addressed below.
- 8.3.1.1 TidbiTs™ (temperature data loggers)
- 8.3.1.1.1 Data from TidbiTs™ help serve as an indicator for the integrity of the SPMD and are critical for determining sampling rates if PRC data are compromised. Results from TidbiTs will help determine if the sampler remained submerged for the entire deployment period or if the sampler was compromised because of exposure to the air.
- 8.3.1.1.2 The Data Reduction SOP describes the processing of temperature data from TidbiTs™. Briefly, to evaluate whether the SPMD sampler was exposed to air at any time during deployment, download and chart the data from the canister TidbiT™. Then download and overlay the data collected from the TidbiT™ that was monitoring air temperature at the same site. Look for any indication where the water temperature shows rapid changes and moves toward the values for the air temperature at the site. This situation likely indicates the SPMD was out of the water and exposed to air for some period.
- 8.3.1.2 Field Replicate Samples
- 8.3.1.2.1 Field replicate samples consist of two or more SPMD canisters deployed side-by-side or located in the same general vicinity. Field replicates help characterize sampling variability and should be included if the project's objectives need estimates of sampling variability. Anticipate a relative percent difference of < 50% for a quality objective.
- 8.3.1.3 Blanks
- 8.3.1.3.1 Blanks are used to characterize levels of contamination at various stages in the measurement system.
- 8.3.1.3.2 Appendix E characterizes various SPMD-specific QC samples that projects have used. A variety of QC samples have been used to meet differing needs. Blanks are used to characterize the magnitude and source of contamination in the various components of the SPMD measurement system. The selection of which blanks to use depends on the project objectives. Consult TSU staff familiar with SPMDs and related contamination issues to help determine which blanks to use. Other QC samples, such as some spike solutions, are also intended to determine sources of contamination in the system. Excluded from Appendix E are PRCs, surrogates, and standards for HRMS analyses (e.g. Extraction Internal Standard - or EIS): these are covered elsewhere in this SOP or in references.

- 8.3.1.3.3 A note on naming conventions: there is great inconsistency in how various SPMD-specific blanks and other QC samples are named. A persistent consequence of this has been confusion and misunderstanding when communicating project needs among all parties involved. Be sure to include a description of each named QC sample in all communications to other staff and labs involved in the project.
- 8.3.1.3.4 Because SPMDs concentrate chemicals in the environment, contamination of the sampling and analytical system usually occurs in the lab and field environment, especially for PCBs, PBDEs, and PAHs. Results from various field and lab blanks can help determine the sources, magnitude, and relative significance of such contamination. The analytical procedures typically used to analyze SPMD extracts usually specify how to address contamination of the analytical system. However, the interpretation of contamination data from field and some lab blank samples is up to the user of the data. Early guidance on the topic from USGS has been interpreted variously by different users of the SPMD systems such that inconsistencies among approaches became important issues when contaminant levels measured in the environment were near levels of detection or environmental concern.
- 8.3.1.3.5 There are various opinions, and controversy, surrounding the interpretation of data showing contamination of the sampling and analytical system. Alvarez (2010) recognized this and suggests that organizations provide guidance to POs and data users in the interpretation of results from field and lab blanks. This SOP is Ecology's method for dealing with these issues.
- 8.3.1.3.6 This SOP addresses the blank contamination issue in the context of planning and conducting studies using SPMDs and is Ecology's guidance on the matter. While Section 10 contains abbreviated procedures for data reduction that include addressing blank contamination, greater detail is available in the Data Reduction SOP.
- 8.3.1.4 Field Blanks
- 8.3.1.4.1 Purpose
- 8.3.1.4.1.1 The purpose, use, and interpretation of field blanks have been controversial topics in the context of SPMDs. Ecology studies have used a various assumptions with, and approaches to, the use of field blanks. These issues are briefly discussed below to provide context for this SOP's selection on the use of field blanks.
- 8.3.1.4.1.2 The purpose of a field blank is to characterize contamination in the sampling and measurement system. A field blank typically consists of the same number of SPMD membranes used in the samples. These blanks are prepared at the same time and spiked identically as the field samples. The levels of contamination in the field blank are assumed to represent the sum of all contamination and de-contamination effects from the varied steps involved in using SPMDs, which are shown in Appendix E.
- 8.3.1.4.1.3 SPMDs are reputed to be potent air samplers (Huckins et al., 2006) to the extent that contributions from air need to be accounted for when using SPMDs in water.

When used in water, the assumption seems to have been that contamination of the SPMDs occurs while the SPMDs are transferred from their argon-filled shipping can to the water where they are deployed for about one month. The period of exposure to air during deployment and retrieval is in the range of 1-4 minutes total.

- 8.3.1.4.1.4 Project goals and objectives should guide the PO in selecting where field blanks should be used. Several aspects need consideration: the spatial extent of the study area, the nature of individual sites, and potential levels of contamination from the air. Field blanks are required for each set of deployments to help meet several needs:
 - 8.3.1.4.1.4.1 Characterize contamination in the measurement system so that results from samples can be appropriately reported.
 - 8.3.1.4.1.4.2 Determine the Limit of Detection (LOD) and Limit of Quantitation (LOQ) associated with each result. The LOD and LOQ should be determined as described by Keith (1991) and Alvarez (2010). The analytical laboratories won't determine the LOD and LOQ, this is generally defined by the PO by using the concentrations and variability of the blanks.
 - 8.3.1.4.1.4.3 Determine the criteria or thresholds for censoring or blank-correcting sample results. In either case, the LOD and LOQ are needed.
 - 8.3.1.4.1.4.3 Help determine the lowest possible concentration of an analyte in water by using the LOD and LOQ values in USGS's spreadsheet calculator (Alvarez, 2010).
 - 8.3.1.4.1.4.5 Determine the initial concentration of PRCs (at time = 0) from which site-specific sampling rates can be determined in conjunction with the final concentration of PRCs (Huckin et al., 2006).
- 8.3.1.5 Number of Field Blanks
 - 8.3.1.5.1 The number of field blanks to use depends on various factors, such as:
 - 8.3.1.5.1.1 Study objectives and intended use of the data: screening level versus compliance versus comparison to other study results.
 - 8.3.1.5.1.2 Target analytes: some are more prone to contamination issues than others.
 - 8.3.1.5.1.3 Analytical methods used: more sensitive methods will likely experience more contamination than less sensitive methods.
 - 8.3.1.5.1.4 Historical experience with target analytes and contamination.
 - 8.3.1.5.1.5 Desired quality and defensibility of the data.
 - 8.3.1.5.1.6 Number and characteristics of sites being sampled.
 - 8.3.1.5.1.7 Available lab budget.
 - 8.3.1.5.2 How results from field trip blanks are used remains a controversial topic: one which includes how to determine the appropriate number and locations of field blanks to use. Earlier guidance for using SPMDs (Huckins, et al., 2006) suggests using a field blank at each deployment site to allow "correction" for site-specific contamination. The 2006 guidance implies that correction is done by subtracting the result of the

blank from the result of the sample at each site. A common variation on the above approach has been to use fewer blanks (to reduce costs) and assume that the contamination from air is the same across all sites within the spatial extent of the sampling program: and then use the “blank-correction” procedure above. Yet the blank-correction of results is authorized in very few analytical methods and involves a more extensive process than using a single blank. The EPA Method 1600 series, such as EPA method 1668 for PCB congeners, requires data from a minimum of ten blanks before determining whether blank-correction can be used.

- 8.3.1.5.3 Concerns about how field blanks are used were acknowledged by Alvarez (2010) who discussed using blanks to determine the LOD and LOQ as described by Keith (1991). The LOD is set at a value that equals the mean value of the blank plus three standard deviations of the mean. The LOQ is set at a value that equals the mean value of the blank, plus ten standard deviations of the mean. The LOD and LOQ are then used to set the criteria for censoring data or for blank-correcting results. This approach uses a statistical treatment of the blank results to determine criteria for censoring or blank-correcting sample results. The statistical treatment of blank results for use in blank-correction negates spurious results (e.g. negative concentrations) and reduces the effects of random errors on final results.
- 8.3.1.5.4 So, this SOP requires that a **minimum of three field blanks** be used during each deployment of SPMDs. This number of blanks is needed to adequately characterize contamination and determine the LOD and LOQ for target analytes. Project Officers may then choose to censor data or conduct blank-correction – in a manner that is more widely accepted and defensible than in previous studies.
- 8.3.1.5.5 Results from the multiple field blanks should also be used to provide the initial concentration of PRCs, rather than using the measured amount spiked into SPMDs during preparation. The use of field blanks to provide the initial concentration for PRCs is supported by Huckins, et al. (2006). Instructions for the most recent USGS Spreadsheet calculator (Version 5.1) states that the initial value for PRCs should not come from the empirical amount added to the SPMDs, but from a fresh SPMD spiked with PRCs (Alvarez, 2010). Ecology has historically used the mass of individual PRCs originally spiked into SPMDs during preparation as the initial concentration of PRCs, so adopting the USGS recommendations results in a change in our procedures. This change will need to be addressed in any studies that aim to compare results to historical results because the historical results are biased. The magnitude and direction of this bias can likely be estimated by re-working the historical data.
- 8.3.1.5.6 Use of a Day 0 blank might also provide the initial concentration for PRCs. Review of field blank and Day 0 blank results for PCBs and PBDEs found no difference between the two blanks (Sandvik and Seiders, 2011). With three field blanks being required for each project to characterize contamination, the value of these field blanks can be increased by also serving as the source for initial PRC concentrations. The three values for initial PRC concentrations will also help characterize the variability inherent in any aspect of SPMDs.

8.3.1.6 Exposure of the Field Blank

8.3.1.6.1 Field blanks should be representative of the way samples are handled, so the handling of field blanks should mimic the handling of project samples. Generally, field blanks are exposed to the air at a site for a period equivalent to the average time the SPMDs are exposed to air during deployment (about 90 seconds), and again during retrieval (about 90 seconds).

8.3.1.6.2 Two methods of field blank exposure have been advocated and debate continues regarding which is the most appropriate method. The two methods are described below: this SOP requires the use of Method A because it best mimics how field samples are handled.

8.3.1.6.3 Method A:

8.3.1.6.3.1 The field blank is constructed and handled identically to a field sample. Membranes for field blanks come mounted on carriers in sealed in 1-gallon cans. The number of membranes used for the field blank is the same as the number of membranes used in field samples. The membranes are removed from the can and placed on a tray covered by clean aluminum foil for the designated time and then returned to the cans. The lids are replaced on the cans and the cans returned to a cooler. The membranes are exposed to the sampling environment (e.g. air, temperature, sunlight, wind, dust) in the same manner as field samples are because they are mounted on carriers and removed from the argon-filled can (argon is heavier than air).

8.3.1.6.4 Method B:

8.3.1.6.4.1 This method has historically been used in Ecology studies because of guidance by USGS. The field blank consists of one or more separate membranes placed inside a single 1-quart can. The individual membranes are often folded or rolled in order to fit into the can. Exposure consists of carefully removing the lid from the can, the membranes remain in the can, and the can is either set down on a stable surface or the can is held by hand and gently moved back and forth in the air. After the designated time for exposure at both deployment and retrieval, the lid is replaced on the can and the can returned to a cooler.

8.3.1.6.4.2 For both methods, the handling of the can and membranes during exposure is similar. The timing for the period of exposure begins when the lid comes off the can and continues until the lid goes back on the can. Carefully reseal the can for the field blank is carefully resealed and returned to a cooler. Ensure each can is labeled. Freeze cans at the earliest opportunity and store frozen between exposures.

8.3.1.7 Field Measurements and Observations

8.3.1.7.1 Field measurements such as temperature and conductivity have QC procedures described in their respective SOPs. Streamflow data are usually obtained from

local, state, or federal governments, either through websites or personal communication: it is presumed that flow data have been through some documented QC process. Some field observations do not have any QC process because of their subjective nature. Yet Field Logs include descriptive information for observations that can help field crews more accurately and consistently state their observations.

8.4 EST Quality Control

- 8.4.1 EST is responsible for the manufacture, preparation, spiking, and possibly extraction of SPMDs. Various QC samples such as blanks, spikes, and spiking solutions are done to help assess contamination during these processes. EST prepares some QC samples routinely and others upon request.
- 8.4.2 EST routinely prepares 4 QC blanks and matrix spikes. These are: Day-zero Dialysis Blank, Fresh Day-zero Blank, Spiking Blank, and Solvent Blank (Appendix E).
- 8.4.3 The Day-zero Dialysis Blank serves as a reference point for contaminant loss and represents background contamination during preparation of SPMDs for field, storage, post-field processing, spiking of membranes, dialysis and Gel Permeation Chromatography (GPC) cleanup. This blank will contain the same number of membranes as used in the field samples and is manufactured at the same time. This blank has been used in some cases to blank-correct results. Previously, EST has prepared this blank as two separate blanks; the Day-zero and the Dialysis blanks. Two separate blanks is an option upon request.
- 8.4.4 The Fresh Day-zero Blank is prepared just prior to dialysis. It contains one (1) membrane and serves as a control during extraction and dialysis. This blank may help in determining sources and levels of contamination. Depending on the parameters designated for analysis, the PO may request this blank to contain the same number of membranes as the field samples to better quantify any contamination.
- 8.4.5 The Spiking Blank may help assess contamination of sample membranes while they are exposed during spiking procedure. The Spiking Blank consists of a single membrane prepared and spiked similarly as other samples (i.e. spiked with PRCs, surrogates, and Extraction Internal Standards). This blank remains exposed to the laboratory environment during the preparation and spiking of other samples. EST will prepare separate Spiking Blank membranes upon request: one for MEL and one for the contract laboratory.
- 8.4.6 The Solvent Blank may be used to assess contamination of the solvent used in the extraction and GPC procedures. This blank consists simply of the solvent used in extraction and GPC and is spiked with PRCs and surrogates at the same time such spiking is done on sample SPMDs. There are no membranes or lipid involved. This blank goes through the dialysis and GPC processes along with the samples.
- 8.4.7 EST will prepare a Membrane Spike in a separate SPMD membrane to avoid having interferes with other analysis such as PCBs and chlorinated pesticides. The spiking solution for the Membrane Spike contains various compounds supplied by

the analyzing laboratories. This was formerly known as the Matrix Spike in Ecology studies yet was not a true matrix spike. The name was changed to prevent the inappropriate and inconsistent treatment of sample results based on the result of this QC sample.

8.4.8 EST will prepare specific blanks to meet method requirements for isotopic dilution using HRMS methods (e.g. PCB congeners with EPA 1668A, and dioxins/furans with EPA 1613). These blanks include a Method Blank and an Ongoing Precision and Recovery blank (OPR). These blanks are identical to the field samples in number of membranes (usually five) and prepared at the same time. The Method Blank is spiked with PRCs and surrogates, yet it is not spiked with Extraction Internal Standards (EIS) as are other samples; the EIS is spiked by the laboratory analyzing the sample extract. The OPR blank is spiked only with the EIS and other analytes specific to the analysis such as labeled and unlabeled PCBs for determining PCB recovery.

8.4.9 EST will prepare other QC samples or blanks upon request. Appendix E shows the variety of sample and QC SPMDs (e.g. blanks) that are used in current and past SPMD studies.

8.5 Laboratory Quality Control

8.5.1 The analytical laboratories include MEL and contract labs. MEL handles analyses for pesticides, PBDEs, and PAHs. Contract labs handle analyses for isotopic dilution methods for PCB congeners and dioxins/furans. Laboratories use a variety of method-specific internal QC practices to evaluate the performance of their analytical systems. Descriptions of these practices are beyond the scope of this SOP, except as noted in the descriptions in Appendix E.

8.5.2 Lab replicate samples have not yet been performed in EAP studies. Lab replicate analyses should be considered if information about lab variability is needed. Laboratory blanks by contract labs are routinely carried out.

9.0 Safety

9.1 Field work done in connection with deploying and retrieving SPMDs should follow protocols described in the Environmental Assessment Program Safety Manual, paying special attention to those parts devoted to driving vehicles, operating boats, and working around the water.

10.0 Data Reduction and Data Management: Abbreviated Procedures

10.1 This section is a summary of procedures for the reduction and management of SPMD data. These procedures are detailed in the Data Management and Data Reduction SOP (EAP079; Seiders and Sandvik, 2013).

10.2 Data Management

- 10.2.1 As described earlier, SPMD projects generate a lot of records and data which must be managed effectively to meet project goals and also to allow other users access to the information. All SOPs and records from SPMD projects are found in the EAP SharePoint site: Passive Samplers SharePoint Repository (http://partnerweb/sites/EAP/passive_samplers/default.aspx).
- 10.2.2 Table 1 in Section 7 is an index of records to be used while conducting SPMD studies. Many of the forms, tables, and records are contained in Excel files as separate sheets. The index shows where templates or examples of individual records are located. The use of these records is required in order to standardize the documentation of our SPMD projects and help allow comparisons among project results. Yet some flexibility can be accommodated in the use of the templates, especially where different formats can improve the use and efficiency of the records. Records not shown in the index can also be added to the data management process as our work with SPMDs further develops. The index also shows where these records are to be stored in the data repository. Descriptions of some records were given earlier in Section 7: Records Management. Others have not yet been described, yet their use and function should be apparent and self-explanatory when viewing the templates and examples.
- 10.2.3 A data repository was created for SPMD projects because EIM was not designed to accommodate modeled or derived data and its supporting information. All SPMD records in electronic format are kept the repository. The repository uses standardized documents and spreadsheets for each project. These files contain all the planning and data reduction information used during an SPMD project. Table 2 in Section 7 shows the general structure of the repository.
- 10.2.4 Most of the required records for SPMD projects are located at Y:\SHARED Files\SPMD\SOP Info\ and on the EAP SharePoint site. Two Excel files contain most of these records, which are also appendices to this SOP. Tables 1 and 2 are also located in the folder above. Filenames for these records are:
- 10.2.4.1 SOP Plan & Deploy templates Appendix A-N May 2016.xlsx.
 - 10.2.4.2 SOP Data Redcn & Repository templates v2 2016.xlsx.
 - 10.2.4.3 SOP Records and Locations Tbl 1 and 2 May 2016.xlsx.
- 10.2.5 As an SPMD project is completed, records in the data repository will be reviewed in the same manner that project data are currently verified in EIM using a defined “QC Process”. First, the index of records will be used as a checklist to show presence or absence of required records. Then, results data in various formats will be verified by comparing against original lab data. These data include SPMD residue results, field notes, model inputs, and other records that have been transcribed or converted from an original format to an end-use format. Initially, about 10 percent of records need to be checked: if errors are found, then an additional 10 percent of records will be checked.
- 10.2.6 After the “QC Process” is complete, the work is documented using the EIM forms, and a notation made that the review was for an SPMD project.

10.3 Data Reduction

- 10.3.1 The analysis and interpretation of SPMD data has been pursued using approaches based on various interpretations of early and developing guidance by USGS and others. One consequence of this has been results that are challenging to compare to other studies' results or to environmental levels of concern due to lack of standard procedures in using SPMDs. SPMD technology is still considered “experimental” or in research phase: EPA or other organizations have not yet deemed SPMD methodology mature or robust enough to be a “standard” method. While SPMD results are often qualified as “estimates”, the qualification often is disregarded in the use and application of the data, even though SPMD guidance cautions users about use of the results.
- 10.3.2 Recent guidance by USGS (Alvarez, 2010) addresses many earlier concerns about reducing and interpreting SPMD results, particularly in the area of blank-correction. Huckins et al. (2006) gave earlier guidance on the analysis and interpretation of SPMD data: some guidance is in a tutorial format (wwwaux.cerc.cr.usgs.gov/SPMD/spmd_overview.htm).
- 10.3.3 The data reduction process here is given as a step by step process contained in Appendix RR-14, located at: Y:\SHARED Files\SPMD\SOP Info\ SOP v4 revision 2016\SOP Data Redcn & Repository templates v2 2016.xlsx.

11.0 References

- 11.1 SPMDs were developed by the U.S. Geological Survey and are now of standardized design, patented, and commercially available only through Environmental Sampling Technologies (EST), St. Joseph, MO. (www.est-lab.com).
- 11.2 Details of SPMD theory, construction, and applications can be found at wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm.
- 11.3 Alvarez, D. A., 2010. Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies. Chapter 4 of: Section D, Water Quality, Book 1, Collection of Water Data by Direct Measurement. Techniques and Methods 1-D4. U.S. Geological Survey, Reston, VA.
- 11.4 Bilhimer, D. and A. Stohr. 2007. Standard Operating Procedures for Continuous Temperature Monitoring of Fresh Water Rivers and Streams Conducted in a Total Maximum Daily Load (TMDL) Project for Stream Temperatures. Washington Department of Ecology, Olympia, WA. SOP No. EQP044. www.ecy.wa.gov/programs/eap/quality.html.
- 11.5 EPA, 2003. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. August 2003. US EPA Office of Water; Office of Science and Technology – Engineering and Analysis Division. Washington DC. EPA Publication # EPA-821-R-07-004.
- 11.6 Huckins, J.N., J.D. Petty, and K. Booij. 2006. Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices. New York, Springer. (An introduction to passive samplers and a detailed description of SPMD technology. Answers to most questions that are likely to arise in an SPMD project can be found here).
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All appendices above are located in three Excel files at Y:\SHARED Files\SPMD\SOP Info\SOP v4 revision 2016, except Appendix G which is part of this SOP document. Filenames for these are:

- SOP Plan & Deploy templates Appendix A-N May 2016.xlsx.
- SOP Data Redcn & Repository templates v2 2016.xlsx.
- SOP Records and Locations Tbl 1 and 2 May 2016.xlsx

Appendix G. Bi-pod Boom Assembly.

- 1.0 **Use of the bi-pod boom assembly**
- 1.1 Use the bi-pod pulley to aid in deployment and retrieval if positioning sampler is difficult.
- 1.2 Bi-pod extension boom advantages.
 - 1.2.1 Bi-pod extension boom will deploy and retrieve further out.
 - 1.2.2 Bi-pod extension boom will lower and rise horizontally rather than dragging across bottom, which may hit a snag.
- 2.0 **Basics on how to set up and operate the bi-pod boom.**
- 2.1 Decide on bank area for bi-pod located near an anchoring point such as a firm tree.
- 2.2 Decide on length of extension needed; usually so the weight and sampler will hang perpendicular from pulley end of extension.

2.3 Attach pulley on hoop using a swivel or quick link connector (Figure 1).



Figure 1. Pulley attached to Bi-pod.

2.4 Insert bi-pod extension pulley feet to tube extensions, then bolt (Figure 2 a and b).



Figure 2. Bi-pod Extension Pulley feet.

2.5 Insert the two tube extensions to length needed, then bolt.

2.6 Bolt on stabilizing cross bar to top or bottom tabs depending on width of leg expansion needed (Figure 3). If short extension or narrow leg expansion is selected, use the top attachment tabs. Alternately, if long extension or wide leg expansion is selected, use the bottom attachment tabs. Note: shorter bolts are needed for the cross bar than for tube extension.



Figure 3. Stabilizing Cross Bar.

- 2.7 Carry to bank and position if not already there.
- 2.8 Tie one end of rope to the hoop opposite of the pulley using a bowline knot (Figure 4). Note the pull should be on the long end of the rope.



Figure 4. Bowline Knot Used to Attach the Bi-pod Extension Top.

- 2.9 Thread cable with prepared canister and weights through pulley. Always have the cable with sampler secured to something in case it slips from your hands. Pulley can be threaded by removing cotter pin, pulley axel, and wheel (Figure 5). Put cable onto wheel and put back together.



Figure 5. Pulley with Cotter Pin.

2.10 Wrap free end of rope several times around the anchor post or tree (Figure 6).



Figure 6. Secure rope to post or tree.

2.11 Position bi-pod by pulling (drawing up) rope or loosening (letting out) rope as needed. Once in position, secure at anchor end.

2.12 Pull or release cable to deploy or retrieve sampler (Figure 7).



Figure 7. Deploying or Retrieving Sampler.

- 2.13 Caution: work the system slowly to allow for weight and balance adjustments.
- 2.13.1 Move the sampler under water at all times so as not to compromise the sample.
- 2.13.2 Lowering the boom by letting out the rope around the tree while at the same time drawing up the cable through the pulley, the sampler will remain underwater but move away from shore. Oppositely, raising the boom by pulling up the rope around the tree while at the same time letting out cable through the pulley, the sampler will remain under water but move closer to shore.
- 2.14 Breakdown is basically opposite of set-up.