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Standard Operating Procedures for Field Water Quality Sampling using Semi-permeable Membrane Devices (SPMDs)

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Acronyms

COC	Chain of custody
ECCC	Environment and Climate Change Canada
EST	Environmental sampling technologies
FWQMS	Freshwater Quality Monitoring and Surveillance
ISO	International Organization for Standardization
POCIS	Polar Organic Chemical Integrative Sampler
PRC	Performance reference compound
QA	Quality assurance
QC	Quality control
SOP	Standard operating procedure
SPMD	Semi-permeable membrane device
USGS	United States Geological Survey

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1.0 Introduction

The following standard operating procedures (SOPs) for the use of semi-permeable membrane devices (SPMDs) in water quality sampling are based on the United States Geological Survey (USGS) Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies (USGS 2010). Guidance from the International Organization for Standardization (ISO) guidelines for passive sampling (Technical Committee ISO/TC 147 2010) was taken into consideration. These procedures are limited to the field application of SPMDs. These procedures do not address study design, deployment infrastructure, health and safety, analytical requirements, or data management and quality assurance (QA)/quality control (QC). Consistent use of these procedures will ensure that the data generated are accurate, scientifically robust, and comparable between samplers, sampling events, and sampling sites.

2.0 General Considerations

SPMDs used in water quality monitoring are intended to measure levels of organic compounds within the water column. SPMDs are susceptible to both uptake and loss of compounds at all stages of use; hence, exposure of SPMDs to air or other sources of potential contamination at times other than during in-water deployment may compromise the sample. Minimizing SPMD exposure must be considered when working with these devices during storage, transportation, handling, field exposure, equipment use, and cleaning.

The following must be considered when using SPMDs:

- The tins within which SPMDs are stored must be tightly sealed at all times; damage to the tins may compromise the seal.

- Exposure to contaminants (vapor, liquid, solid) outside of the intended sampling period will compromise the sample.

- SPMDs are inactive at approximately –20°C and should always be kept at a temperature of less than 0°C outside of deployment. This is particularly critical once the SPMDs have been retrieved, as activity associated with the organic matter and biological organisms attached to the SPMDs may alter organic compounds.

- Cleanliness, cleaning standards, and equipment standards are essential for preventing contamination.

- Detailed documentation is critical in supporting the QA/QC of samples, data integrity, and the interpretation of results.

Many events that occur prior to, during, and after sampling may compromise the integrity of the sample and the associated data. A sample may be considered compromised if:

1. the membrane is not intact (i.e., damaged);

2. the membrane has been exposed to contamination;

3. the deployed membrane has not remained submerged throughout the deployment period (e.g., a sample exposed to air or submerged in sediment is not representative of water); and

4. the deployed membrane has shifted location during deployment or has not remained within the same general vicinity of the original sample location (e.g., it was swept downstream of additional sources of water or potential water resource stressors).

3.0 Equipment

3.1 SPMD Membranes

SPMDs are designed to mimic biological organisms in the passive accumulation of compounds. Each membrane is composed of lay-flat, low-density polyethylene tubing that contains a thin layer of a pure, high-molecular-weight lipid (triolein). A single membrane that is to be deployed in the field is loaded onto a stainless steel “spider” or carrier. The carrier is placed in a stainless-steel deployment canister, which may house up to five spiders. One sample consists of a composite of three membranes. Figure 1 depicts a membrane, spider, and canister.

Figure 1. Preparing for the field deployment of a membrane and spider (top right) and canister (bottom right).

SPMDs are manufactured by Environmental Sampling Technologies (EST; http://www.est-lab.com/) and shipped to Environment and Climate Change Canada (ECCC) in clean tins (Figure 2). ECCC receives membranes that are used in the following five ways: as samples, field blanks, travel blanks, dialysis blanks, and spike blanks (Table 1). All membranes, apart from the spike blank, are spiked by EST with 10 µg of fluoranthene-d10, 10 µg of anthracene-d10 and 1 µg of dibenz [a,h] anthracene-d14. These performance reference compounds (PRCs) are used to calibrate for differences in conditions (e.g., temperature, flow, biofouling) between sites and over time; the concentrations of these compounds within the SPMDs are used to calculate the time-averaged concentration of organic compounds in the water column.

Figure 2. Semi-permeable membrane device tins. The large tin is representative of a sample membrane, the medium tin represents a field blank, and the small tin represents travel/dialysis/spike blanks.

Table 1 – Semi-permeable membrane device types and applications
Three membranes are treated as one composite sample or blank.

Membrane Type	Number of Membranes	Handling	Application
Sample	3	Deployed in water	Measuring levels of dissolved compounds in the water column with PRCs. The samples are deployed in canisters that are attached to a deployment array (see the ECCC FWQMS-AA SOP *Deployment Arrays*), which consists of an anchored, suspended float in deep waters or a weighted block in shallow waters.
Field Blank	3	Transported with the sample and opened during field deployment and retrieval	Measuring the exposure of the sample during deployment and retrieval with PRCs. Each sample has a companion field blank (i.e., one field blank for each site and sampling event), which is used to correct sample concentrations for exposure that has occurred outside of the water column.
Travel Blank	3	Transported with sample and field blank – unopened	Measuring the exposure of sample and field blanks during transport – with PRCs. Each QC sampling event (i.e., approximately 10% of sampling events) includes the collection of triplicate samples with one companion field blank and travel blank.
Dialysis Blank	3	Remains in the freezer – unopened	Measuring background levels of compounds upon manufacture with PRCs. Dialysis blanks for each SPMD lot (i.e., a minimum of three for each batch from EST) are retained in storage until the analysis of samples and companion blanks. Concentrations of PRCs in these blanks are used in the calculation of water concentrations.
Spike Blank	3	Remains in the freezer – unopened	Measuring the background levels of compounds upon manufacture – without PRCs. Spike blanks for each SPMD lot (i.e., a minimum of three per batch from EST) are retained in storage until the analysis of samples and companion blanks.

PRC = Performance reference compound; ECCC = Environment and Climate Change Canada; FWQMS = Freshwater Quality Monitoring and Surveillance; SOP

= standard operating procedure; QC = Quality control; SPMD = semi-permeable membrane device; EST = Environmental Sampling Technologies.

Table 2 – Supporting equipment

Supporting Equipment	Equipment Description	Application	Equipment Requirements
Temperature logger (e.g., HOBO®)	A portable data logger used to record "real-time temperature".	Monitoring the temperatures to which SPMDs are exposed during both deployment and sample transit, including prior to deployment and after retrieval. Attached to a stainless-steel SPMD canister during deployment.	HOBO® (http://www.onsetcomp.com/products/software): Connect the unit to a HOBO® Waterproof Shuttle with Coupler (part # COUPLER2-C) prior to operation and enable temperature logging at 10-minute intervals using HOBOware software.
Trackpacks (e.g., NorthStar Science and Technology)	A small removable unit allowing for GPS tracking.	Monitoring field units in remote locations. GeoFences are set up around SPMD deployment arrays to trigger warning emails if the units have moved. They are attached on top of a buoy, facing skyward.	NorthStar Science and Technology (https://www.northstarst.com/): Open an account with a NorthStar representative to activate hardware. Set up airtime requirements for active units. These devices use the Globalstar satellite network.
Multi-probe (e.g., YSI® Sonde)	A multi-probe unit that allows for discrete or unattended sampling of several water quality parameters, including water temperature, specific conductance, pH levels, dissolved oxygen, and turbidity.	Measuring water conditions at the time of SPMD deployment and retrieval.	YSI® (http://www.ysi.com/index.php): Units must be calibrated and maintained in accordance with the YSI user's manual. Calibration of the unit is completed at the beginning of each field trip and on every 5th day of unit use.
Velocity meter (e.g., Sontek® Flowtracker)	A wading velocity measurement device that calculates discharge using two- or three-dimensional currents.	Calculate velocity at 60% depth at the deployment sites. Measurements are taken at the time of deployment and retrieval during flow conditions.	Sontek® Flowtracker (http://www.sontek.com/): Follow the operating procedures detailed in the user's manual. Accompanied by a hand level and wading rod.
Hand-held weather meter (e.g., Kestrel)	A hand-held "pocket weather meter" allowing users to measure a number of environmental conditions, including wind speed and air temperature.	Measure weather conditions on site during the deployment and retrieval of SPMDs.	Kestrel (http://kestrelmeters.com/): Sensors are factory calibrated. Consult the instruction manual for maintenance requirements.

Additional equipment is listed in Appendix A.

SPMD = Semi-permeable membrane device; ECCC = Environment and Climate Change Canada; FWQMS = Freshwater Quality Monitoring and Surveillance; SOP = standard operating procedure.

4.0 Methods

4.1 Storage and Transportation

- SPMDs are more proficient at sampling air than water; the membranes should be kept at temperatures between 0°C and –20°C at all times when not deployed (USGS 2010). Store SPMDs (Figure 2) in a freezer (preferably in temperatures of –20°C) while not in use, as lower temperatures inhibit the uptake and loss of volatile organic compounds, including PRCs, from SPMDs. Freezer storage is particularly critical once the SPMDs have been retrieved, as the activity associated with organic matter and biological organisms attached to the SPMDs may alter the organic compounds. Temperatures below –20°C may cause the membranes to become brittle and prone to breakage.

- Transport the SPMDs in their original sealed tin in a cooler with wet (blue) ice packs and a temperature logger. Do not use dry ice, as it may cause the membranes to become brittle and susceptible to cracking. The ice packs should be placed in plastic bags in case of leakage. As best practice, SPMDs should be frozen at –20°C for a minimum of 24 hours prior to shipping.

- Transport the deployment canisters in clean packaging (e.g., a clean poly bag or garbage bag).

- Denting of the tins may damage the argon seal and expose the membranes. Take adequate measures to prevent damage to the cans (i.e., using packing materials and/or tightly packed ice packs).

4.2 Prior to Deployment/Retrieval

- Clean the deployment canisters following the SOP provided by EST (detailed in Appendix B). Once cleaned, store the canisters in their original packaging, if possible. Wrap the canisters in a clean poly bag. If a float is being used as part of the array, clean the float using the same procedure.

- Activate the HOBO® temperature logger by programming it to record the temperature every 10 minutes (i.e., delayed logging) using the HOBO® Shuttle and Onset software.

- Activate Trackpack.
- Check the array location.
- Select the SPMDs (samples and companion blanks) from the same lot number (assigned by EST upon manufacture) and label all tins with the following: sample number, site name, and sampling (deployment) date.
- Ensure that the sample tins and associated blanks used for the previous deployment are packed for subsequent retrieval.
- Print and populate the field sheets (Appendix C).
- Pack clean deployment canisters.
- Pack coolers immediately before departure. Remove the SPMDs from the freezer and pack them with wet ice packs in coolers, confirming that the SPMD lot numbers match the samples/field blanks/trip blanks for each site. Add a temperature logger to the cooler.
- Calibrate the YSI® Sonde.

4.3 Field Methods

4.3.1 Deployment

Upon arrival at the site, take multi-probe readings of water pH levels, specific conductance, dissolved oxygen, temperature, and hand-held weather readings. Complete the field sheets.

1. Stage for SPMD exposure. Ensure all working surfaces and equipment are clean, such that the SPMDs are not exposed to contaminants other than those in the air and water. Lay out the tins (sample and field blanks) and equipment (canisters, temperature logger, church key, stopwatch, camera, rubber mallet, etc.) in a manner that is conducive to efficient SPMD transfer (i.e., limiting the time of exposure to air and precipitation). Assign roles among the team – designate a crew member to be gloved for SPMD carrier handling, as this individual is not to touch other surfaces (“clean hands”), including the canisters and tins; the other crew members should be responsible for handling the tins, canisters, timing, photography, notetaking, etc.

2. Prior to deployment, slightly pry open the lids on the sample and field blank tins using a church key. Prepare the stopwatch and begin timing upon simultaneously removing the lids from the tins. Minimize sample and field blank exposure to precipitation and direct sunlight, as this will rapidly degrade some polycyclic aromatic hydrocarbons. An umbrella may be used

to shelter the membranes, particularly if deployment is unexpectedly delayed.

3. **DO NOT HANDLE** the membranes. Do not use bug spray, lotion, or other items that may contain organic compounds. The “clean-hands” crew member should wear new nitrile gloves and load the carriers onto the centre spindle of a clean deployment canister as rapidly as possible, without compromising the sample or the health and safety of the field crew. Stainless-steel or Teflon spacers may be used to separate individual carriers within a canister. If a membrane is not properly attached to the carrier, or if the carrier will not fit onto the canister spindle, carefully remove the membrane from the carrier and place it loosely into the deployment canister; try to handle the membrane by the end loops. Note this on the field sheet.

4. Screw the canister lid tightly onto the canister. Matching the mounting ring on the lid with its opposing ring on the canister body, secure and fasten the lid to the canister using a zip tie, stainless-steel carabineer, or other fasteners.

5. Attach the temperature logger to the sampling canister ring.

6. Attach the deployment canister to the sampling array.

7. As the deployment canister enters the water, simultaneously replace the lids of the empty tins and the field blank tins and stop the timer. With care, immediately reseal the tins using a rubber mallet on the edges of each lid. Return the tins to the cooler. These tins will be used to retrieve the sample in the following month.

8. Fill in the field sheet and document the field blank exposure time, as well as any damage or possible membrane contamination.

4.3.2 Retrieval

Upon arrival at the site, take multi-probe readings of water pH, specific conductance, dissolved oxygen, temperature, and hand-held weather readings. Complete the field sheets. After doing so, complete the following steps:

1. Stage for SPMD exposure as in Section 4.3.1, “Deployment”.

2. Ensure that a plan is in place to safely and effectively remove the canisters from the water (e.g., secure the deployment array/float).

3. Prior to sample retrieval, prepare the tins as in Section 4.3.1, “Deployment”. Prepare the stopwatch and begin timing when the lids from the tins are removed and the canisters simultaneously breach the water’s surface. Remove the fasteners from the canister (e.g., cut the zip tie).

4. Handle the membranes as indicated in Section 4.3.1, “Deployment”. The “clean-hands” crew member should wear nitrile gloves and carefully remove the carriers from the canister and place them in their original tins. If the carriers are covered with excessive sediment, gently shake them to dislodge the sediment prior to placing them in the tin. Note this on the field sheet.

5. Take a photo of one of the membranes prior to placing it in the tin. This photo may be used to verify biofouling and sediment exposure.

6. Simultaneously replace the lids of the tins and stop the timer. Carefully and immediately reseal the tins using a rubber mallet on the edges of each lid. Return the tins and the accompanying temperature logger to the cooler.

7. Fill in the field sheet and document the field blank exposure time and any damage to – or possible contamination of – the membranes. Deployment canisters may be stored in a polybag or garbage bag and transported back to the laboratory or warehouse for cleaning. Cleaning is much easier if the debris on the canisters is not allowed to dry.

4.3.3 Field Observations

Upon arrival to the site, take multi-probe readings of water pH levels, specific conductance, dissolved oxygen, temperature, and hand-held weather readings. Complete the field sheets.

Field observations are recorded on the SPMD field sheet (Appendix C). Weather, flow velocities, and site-specific conditions and characteristics (e.g., wind, precipitation, fume exposure, membrane damage, sediment exposure, and change in deployment array location) should be noted, as they may affect the uptake or loss of compounds from the sample and field blank membranes and will be critical to data interpretation. The following should be noted in the field:

- **Weather:**
    - **Cloud cover:** Estimated percent cloud cover; in such conditions, photodegradation of organic compounds can occur.
    - **Wind:** Wind speed and direction; SPMDs are efficient air samplers and exposure to wind and airborne contaminants will affect the uptake and loss of compounds.
    - **Temperature:** Air temperature; temperature affects the rate of uptake and loss of organic compounds (i.e., higher temperatures increase the rate of exchange).
    - **Precipitation:** Rain or snowfall; SPMDs may absorb precipitation.

- **Hydrological observations:**
    - **Flow:** Flow velocity; the rate of flow affects the rate of compound exchange between the water and the SPMD. General observations regarding changes in flow and the location of the deployment array are noted.
    - **Depth:** Water depth; the depth of the canister relative to the water's surface and the bed may be used to interpret water temperature, sediment exposure, and photodegradation.
    - **Ice conditions:** Ice thickness; the thickness of the ice and the depth of the overlying water may be used to interpret water temperature and photodegradation, as well as the exposure of SPMDs to ice-borne contaminants.
- **Membrane condition and contamination:**
    - **Biofouling:** Biofouling class; the accumulation and growth of organic matter/suspended sediment and algae on SPMDs can alter the exchange of compounds between the water and the membranes, and it can also result in the bacterial degradation of organic compounds. Qualitative estimates of biofouling are recorded using five classes, which range from 0 (no apparent biofouling or suspended sediment accumulation) to 4 (a high degree of biofouling or suspended sediment accumulation; i.e., the film's surface is obscured by thick growth/accumulation).
    - **Bed sediment exposure:** Sediment exposure class; in shallow waters, SPMDs may become exposed to or buried by bed sediments, reducing the degree to which the membranes represent water samples. Qualitative estimates of bed sediment exposure are recorded using five classes, which range from 0 (no apparent bed sediment exposure) to 4 (when more than three quarters of the membrane's surface area is exposed to bed sediment).
    - **Membrane integrity:** Damage to the SPMDs or failure of the tin seal; the membranes may tear, the tins may become dented, and the seal may break. Membranes and tins are inspected, and the conditions that may compromise their integrity are noted.
    - **Contamination:** Contamination originating from the air, sediment, equipment, or field practices are noted.

4.3.4 Site-Specific Conditions

Site conditions will affect the nature of the water sampled by the SPMDs and will have implications for the employed deployment and retrieval techniques. SPMDs

are typically deployed within the thalweg of the water body to represent the dominant water conditions in the channel, above the bed and in consideration of changing water levels to avoid contamination of the membranes with channel sediments, in shaded areas whenever possible to limit photodegradation of compounds, and away from stagnant waters to limit fouling of the membranes. Site-specific considerations that must be kept in mind to ensure the integrity of a sample during the sampling process thus include:

- **Water depth:** SPMDs may be suspended from the surface by an anchored buoy in deep waters or deployed on the bed in shallow waters.
- **Flow velocity:** Swift-flowing waters versus slow-flowing waters, which affect the rate with which the compounds are exchanged between the water and membranes.
- **Access:** Access may be by floatplane, boat, or wading.
- **Season:** SPMDs may be suspended under ice.

4.3.4.1 Open-Water Rivers

The deployment and retrieval of SPMDs in large, swift-flowing rivers typically require access via motorboat or floatplane and working with an anchored buoy (ECCC 2018a). The deployment location should be approached from a downstream position, whether motoring by boat or taxiing by floatplane. The motor should be turned off a minimum of 20 m away from the buoy and the craft should be allowed to drift toward the deployment array, if the water current allows. If the motor is left running during SPMD deployment or retrieval, this should be noted on the field sheet.

If a grappling device is used to capture the buoy, care should be taken to not breach the water's surface with the canisters prior to crew preparation for retrieval. A minimum lead time of 10 minutes should be taken to ensure that the fuel residue dissipates before exposing the SPMDs or opening the tins. If the motor must remain running, note this on the field sheet.

Equipment and sample loss occurs rapidly in swift-flowing rivers; take appropriate measures to avoid the loss of equipment and samples. Upon departure, allow the craft to drift downstream of the buoy prior to restarting the motor; maneuver clear of the buoy.

4.3.4.2 Rivers Under Ice

The deployment and retrieval of SPMDs in large rivers in the winter typically require access via snowmobile or helicopter, as well as working with samples that are suspended under ice (ECCC 2018a). The deployment location should be approached from downwind and the motor should be turned off a minimum of 20 minutes prior to SPMD deployment or retrieval.

Snow may need to be cleared from the deployment location. An electric auger, hand auger, or ice chisel should be used to create or clear an opening in the ice. If a gas-powered auger must be used, a minimum lead time of 20 minutes should be taken to allow the fuel residue to dissipate before opening the tins and exposing the SPMDs. If a gas-powered auger is used, note this on the field sheet. Clear the hole of all slush and ice prior to the deployment and retrieval of canisters.

4.3.4.3 Streams

The deployment and retrieval of SPMDs in streams typically requires access by wading and working with samples that have been deployed on or near the bed (ECCC 2018a). Proper scouting of the deployment location will reduce potential delays during deployment and retrieval (i.e., it will limit the amount of time the SPMDs are exposed to air), as well as health and safety mishaps with field crew.

Care must be taken to ensure that the sample is not compromised when wading. Approach the deployment array from downstream and take multi-probe measures upstream of the sampler. In streams with soft sediments and/or slow-moving water, extra care must be taken when approaching the array, as movement of the sampling personnel may disturb/resuspend sediments, exposing the SPMDs to a sediment plume and potentially compromising the sample. If the deployed devices are secured with a cable, caution should be exercised when wading in or out of the stream to avoid the cable. Arm-length gloves may be necessary in cooler waters, especially if water levels have risen since deployment. Changes in water levels may result in exposure of the SPMDs to air, compromising the sample.

4.3.4.4 Wetlands

Deployment and retrieval of SPMDs in wetlands typically require access by a small, non-motorized zodiac, as well as working with samples that have been deployed with an anchored buoy. Extra care should be taken in wetlands where waters are stagnant, as the exposure of SPMDs to disturbed/resuspended sediments may compromise the sample.

4.4 After Deployment/Retrieval

- In the field, following deployment and retrieval, immediately return all blanks and samples to the cooler with ice packs and accompanying HOBOs®. Upon returning to the laboratory or warehouse at the end of the day, the SPMDs should be immediately returned to the freezer (preferably in temperatures of –20°C), along with the appropriate temperature loggers, as per the protocol outlined in Section 2.0, “General Considerations”.

- Ensure the dialysis and spike blanks are kept frozen at all times and submitted for analysis alongside the samples, field blanks, and trip blanks.

- Clean the deployment canisters following the SOP provided by EST Labs (Appendix B). Clean the canister immediately following retrieval for efficient

cleaning and place the canister in a clean polybag; then, return the canister to its original – or to an alternative – storage box.

- Organize and backup field sheets and photos as soon as possible.

- Download and backup the temperature logger data once the membranes are returned to a freezer.

- Initiate and populate the tracking files (see Section 4.5).

- If shipping from the site is necessary, find the most direct and efficient route possible. Longer travel times result in higher temperatures, which may affect the membranes. All coolers should be packed with sufficient ice packs and appropriate HOBOs® and blanks. Use packing material, if necessary, to prevent damage to the tins.

- When shipping to the laboratory for analysis, pack the samples and companion (field, travel, dialysis, and spike) blanks in coolers with ice packs. As a best practice, the samples and blanks should be frozen at –20°C for 24 hours prior to shipping. Contact the laboratory for chain of custody (COC) forms, shipping directions, and contacts. Provide the laboratory with the tracking information and confirm receipt.

4.5 Record Keeping

- **Field Sheets:** Retain a hardcopy in a binder organized by year and site. Create an electronic copy and store it in a secure location.

- **Photos:** Store copies of the membrane photos with the associated field sheet.

- **Deployment and retrieval tracking:** Organize a spreadsheet that displays planned, deployed, and retrieved membranes. Populate a separate spreadsheet with sample information and all related field and laboratory notes. This ensures easier access to sample numbers and provides a quick overview of any occurrences that may have compromised a sample, or that may be relevant to data interpretation. Any exceptions, such as why a specific sample may not be usable, should be flagged or noted in this document.

- **Temperature loggers:** Create a readout of the logger using the appropriate software (e.g., HOBOware). Export the data onto a spreadsheet. Calculate the mean, maximum, and minimum temperatures for the time between deployment and retrieval, then enter these data into the sample tracking spreadsheet along with the field multi-probe measures.

- **Laboratory tracking:** Print hard copies of all data and associated COC forms received from the laboratory. Keep the electronic copy in a secure

place. Organize and retain communications with the laboratory that pertain to sample processing and tracking.

5.0 Field QA/QC

SPMDs are used to measure concentrations of organic compounds within the water column. SPMDs are susceptible to both compound uptake and loss at all stages of use; thus, exposure of the SPMDs to air or other sources of potential contamination beyond in-water deployment has the potential to compromise the sample. An appropriately quality-assured and quality-controlled program safeguards the integrity of the sample and the information attained from it.

QA/QC of the SPMD field program is captured in the design and delivery of the program. This section addresses those QA/QC measures that are taken with respect to the field program; it does not address data or laboratory QA/QC.

The field QA/QC program aims to ensure that i) exposure of SPMDs to contaminants outside the water column (i.e., outside the period of deployment) is minimized; and ii) contamination/exposure of the SPMDs outside of water sampling is measured. As such, the program includes the application of SOPs by trained personnel, as well as the collection of blanks.

5.1 QA/QC Program Design

The SPMD program includes the following QA/QC measures:

- Each sample has a companion field blank (Table 1).
- At a minimum, all samples and blanks are labelled with their site name, deployment date, retrieval date, sample type, and other specifications, as appropriate (e.g., PRC type).
- A minimum of 10% of sampling events are QC events, which include the collection of a full suite of QC samples (Table 1):
    - triplicate samples;
    - a single field blank; and
    - a single trip blank.
- QC sampling events are cycled through each of the sites on an annual basis:
    - e.g., for a program that includes sampling at nine sites on a monthly basis over a total of 7 months in a given year (excludes shoulder seasons), one QC event will occur at each site over the course of the

year – this is particularly important where multiple teams/agencies are collecting samples across the region being monitored.

- Review of field and trip blank data to determine if the methods need to be modified:
    - e.g., trip blank hits may indicate a need to decrease the potential for contamination during transport; and
    - e.g., field blank hits that exceed expectations may indicate the need to decrease the exposure time or conditions during the deployment/retrieval of samples).
- The retention and analysis of dialysis and spike blanks, which provide measures of background concentrations of organic compounds upon manufacture (Table 1).
- The selection of a laboratory that meets the analytical requirements of the program, such as the application of QA/QC measures, including:
    - analysis of method blanks, method spikes, and laboratory replicates;
    - the use of appropriate calibration standards and methods; and
    - the use of appropriate surrogates and recovery acceptance criteria for organics.

Data management and processing procedures, including QA/QC, are outlined in ECCC 2018b.

5.2 Methods

The quality of SPMD samples and their associated information may be assured through the application of SOPs by trained personnel. These specified procedures are to be applied to both samples and blanks.

These procedures, when adhered to, should ensure that samples (including QC samples) are not exposed to contaminants during (or resulting from) storage, transportation, handling, field exposure, equipment use, and cleaning. If exposure does occur, QC samples should be collected following the SOPs listed in Section 5.1, “QA/QC Program Design”; this will ensure that the level of exposure may be measured, allowing for correction.

In short, SPMDs:

- shall be handled as specified in the SOP;
- must be stored under tight seal and without damage;

- must not be exposed to contaminants (vapor, liquid, or solid) outside of the intended sampling period; and,
- SPMDs should be kept at a temperature between -20°C and 0°C at all times outside of deployment.

5.3 Record Keeping

Detailed documentation is essential when supporting QA/QC. Standard, comprehensive, and secure record keeping is essential for sample tracking, data integrity, and interpretation of the results.

Data records shall include:

- sample number;
- site name;
- sampling date (deployment and retrieval);
- PRC type (10 µg, 2 µg, or photodegradation);
- lot number (of the SPMDs received from the manufacturer);
- sample type (sample, field blank, trip blank, dialysis blank, or spike blank);
- GPS coordinates (latitude and longitude);
- water depth (if possible, at deployment and retrieval);
- flow rate (if possible, at deployment and retrieval);
- physical measures (water temperature, pH level, dissolved oxygen, and turbidity at deployment and retrieval);
- air exposure time;
- water temperature (logged mean, minimum, and maximum);
- analysis date (sent to/received from the laboratory);
- number of films per sample; and
- comments – handling/damage/exposure of films, biofouling (degree/class), sediment exposure, shipping concerns, and laboratory comments (e.g., loss of sample).

This information will be used in data QA/QC and interpretation, and it can also be used to identify samples that have been compromised by such factors as:

- damage;
- contamination;
- changes to sampling conditions (e.g., samples exposed to air or submerged in sediment are not representative of those obtained in water); and,
- changes in location during deployment (e.g., swept downstream of additional sources of water or potential water-resource stressors).

Data records shall be backed up on a regular basis as a best practice.

5.4 Field Audits

Field audits are conducted to ensure that SOPs are followed. Audits should take place at a minimum of twice a year – once during open-water sampling and once during under-ice sampling. If multiple crews are conducting the sampling, an annual field audit should take place with each crew. A checklist (Appendix D) is completed during each audit. Practices that do not adhere to the SOPs are noted, including follow-up actions and outcomes. The results of the audit are shared with the crew members that participated in the audit.

6.0 References

Technical Committee ISO/TC 147. 2010. *Water Quality – Sampling – Part 23: Guidance on Passive Sampling*. DRAFT. pp. 23.

United States Geological Survey. 2010. *Guidelines for the Use of the Semipermeable Membrane Device (SPMD) and the Polar Organic Chemical Integrative Sampler (POCIS) in Environmental Monitoring Studies*. Accessed March 27, 2018. *http://*pubs.usgs.gov/tm/tm1d4/pdf/tm1d4.pdf.

Environment and Climate Change Canada (ECCC). 2018a (*in press*). Standard Operating Procedures for the Deployment of Anchoring Arrays for Water Quality Sampling Devices in Large Rivers. ISBN XXX-X-XXX-XXXX-X. Environment and Climate Change Canada, Water Science and Technology, Freshwater Quality Monitoring and Surveillance, Athabasca Arctic Basin, Saskatoon, SK, 8p.

Environment and Climate Change Canada (ECCC). 2018b (*in press*). Standard Operating Procedures for Management and Processing of Water Quality Data Collected using Semi-permeable Membrane Devices (SPMDs).ISBN XXX-X-XXX-XXXX-X. Environment and Climate Change Canada, Water Science and Technology, Freshwater Quality Monitoring and Surveillance, Athabasca Arctic Basin, Saskatoon, SK, 38p.

Appendix A. Equipment List

Primary Equipment List	***Quantity***	✓
SPMDs for Retrieval		
Sample	As needed	
Field Blank	As needed	
Trip Blank	As needed	
SPMDs for Deployment		
Sample	As needed	
Field Blank	As needed	
Trip Blank	As needed	
Icepacks (wet/blue)	As needed	
Cooler(s)	As needed	
Deployment Canisters (cleaned with solvents and bagged)	As needed	
Clean work surface Supplies (to use while handling SPMDs and canisters)	As needed	
Temperature Logger (i.e. HOBO temperature loggers)	1/site	
Nitrile Gloves	Multiple	
Paint Can Opener	2	
Rubber Mallet	1	
Umbrella	1	
Field Sheet	As needed	
Stopwatch	1	
Camera	1	
Depth Sounder	1	
GPS	1	
Program Specific Array Equipment	As needed	
Supporting Equipment List		
Multi-probe meter (e.g., YSI Sonde)	1	
Flow velocity meter (e.g., SonTek Flow Tracker)	1	
Weather meter (e.g., Kestrel Pocket Weather Meters)	1	
GPS tracking (e.g., Trackpacks)	1/site	

Appendix B. Standard Operating Procedure — Cleaning of SPMD Canisters

Objective

The purpose of this SOP is to detain the procedures for cleaning of the SPMD deployment devices before and after field deployment. These procedures are based on Standard Operating Procedure (SOP) E-13 developed by Environmental Sampling Technologies Ltd. (EST), which manufactures the SPMDs and is a supplier of the deployment canisters and film carriers. These procedures are adhered to by Environment Canada, unless otherwise specified.
These procedures apply only to the deployment devices (i.e., stainless steel canisters). The carriers (i.e., stainless steel spiders that carry the films) are cleaned and loaded with films by EST and returned to their sealed tins upon retrieval.
Cleaning is to take place in a clean environment where exposure to contaminants is minimized (e.g., lab, clean space in field/warehouse lab). The use of acetone and hexane must take place in a well-ventilated area (preferably within a fume hood).

Equipment and Supplies

- free-rinsing, non-perfumed laboratory detergent (e.g., Fisher brand Sparkleen I)
- hot water bath (e.g., stainless steel sink)
- drainage rack
- firm, bristled brush, scour pad
- chemical-safe squirt bottles
- PPE
- ACS (American Chemical Society) certified nanograde or pesticide grade acetone (e.g., A19-A Acetone, Fisher Chemical 27 L-5593)
- high-resolution gas chromatography-suitable hexane (e.g., H307-4 n-hexane, Fisher Chemical 126 L-11570)
- bowls/trays (preferably stainless steel if they are to come into contact with the canisters) to capture excess solvent
- clean paper towels upon which to dry solvent-rinsed canisters
- new plastic bags / polybags
- rigid storage container
-

Procedures

Upon Receipt from Manufacturer:

1. Dismantle the deployment devices, if necessary, and soak in a hot water bath using free-rinsing, non-perfumed laboratory detergent (such as Sparkleen 1).

2. After soaking in the detergent solution for several minutes, scrub each piece thoroughly with a firm, bristled brush, then rinse with hot water and set in a drainage rack to dry.
3. Once dry, place the deployment devices in new plastic bags and place in designated, sealed, rigid storage container (i.e. Rubbermaid) until cleaning prior to deployment.

Before Deployment (as close to deployment date as possible; no more than 2 weeks):

1. Remove the deployment devices from the designated storage container they have been stored in. Soak and rinse the pieces in a hot water bath, then set in a drainage rack to dry. Ensure that the bath (e.g., sink) has been cleaned with free-rinsing, non-perfumed laboratory detergent and rinsed with hot water prior to rinsing the deployment devices.
2. Once each piece is dry, rinse each one with ACS (American Chemical Society) certified nanograde or pesticide grade acetone to remove water, and then allow to dry.
3. Rinse each piece thoroughly with hexane (high-resolution gas chromatography-suitable), then allow to dry.
4. Place and seal the deployment devices in new polybags until the time at which they are deployed. Store the bagged devices in a location where the bags will not be damaged and where their exposure to contaminants will be minimized.

After Deployment:

1. The deployment canisters may be covered with deposits (algae, minerals, micro-organisms, etc). Storage of the devices in plastic bags upon retrieval (prior to cleaning) will maintain a high moisture level and, thereby, ease future cleaning effort.
2. When ready for cleaning, disassemble the devices, if necessary, and soak the pieces in a hot water bath using free-rinsing, non-perfumed laboratory detergent for approximately 10 minutes. The devices may need to soak for a longer period of time if deposits have dried or are particularly resistant to cleaning.
3. Using a firm, bristled brush, scouring pad or small wire brush, remove as much of the deposits as possible. If the deposits are still resistant to removal, refer to and follow the EST SOP E-13 for cleaning using an acid bath or muffle furnace. Rinse the pieces with hot water and set in a drainage rack to dry.
4. Place the deployment devices in designated, sealed, rigid storage containers until the time at which they are cleaned before deployment. Store the devices such that their exposure to contaminants will be minimized.

Appendix C. SPMD Field Sheet

SPMD FIELD SHEET
Environment Canada

SITE NAME: _____

GPS COORDINATES: _____ N _____ W DATUM: _____

DATE OF: **DEPLOYMENT**_____ **RETRIEVAL**_____

CREW: DEPLOYMENT_____

RETRIEVAL_____

HOBO # _____

SPMDs STANDARD Lot #: _____ Triplicate ☐ yes ☐ no

EXPERIMENTAL ☐ 2 ug ☐ Photo Lot #:_____ Triplicate ☐ yes ☐ no

SAMPLE No. STND SAMPLE _____

STND FIELD BLANK_____ STND TRIP BLANK_____

EXP SAMPLE _____

EXP FIELD BLANK_____ EXP TRIP BLANK_____

SITE DRAWING (Include location of buoy and other samples, landmarks, and **buoy displacement**)

	DEPLOYMENT	**RETRIEVAL**
WEATHER CONDITIONS		
	☐ **See "Retrieval" – Previous Sample**	
AIR TEMP (^{O}C)		
WIND STRENGTH		
PRECIPITATION		
CLOUD COVER (%)		
OTHER SAMPLES		
	☐ **See "Retrieval" – Previous Sample**	
WATER QUALITY	☐ PAH ☐ Metals ☐ Nutrients ☐ Other _____ Time: Sample #:	☐ PAH ☐ Metals ☐ Nutrients ☐ Other _____ Time: Sample #:
OTHER (i.e., biosampler)		

	DEPLOYMENT	RETRIEVAL
SITE AND FLOW CONDITIONS		
	☐ **See "Retrieval" – Previous Sample**	
WATER DEPTH (m) (Effective)		
ICE THICKNESS (m)		
FLOW (m/s)		
HAS ARRAY MOVED?	☐ yes ☐ no Details/GPS Coord.:	☐ yes ☐ no Details/GPS Coord.:
AUGER BOAT MOTOR	☐ electric ☐ gas ☐ running ☐ off Approx. time for fumes to dissipate:	☐ electric ☐ gas ☐ running ☐ off Approx. time for fumes to dissipate:
FIELD MEASUREMENTS		
	☐ **See "Retrieval" – Previous Sample**	
TIME (local time zone)		
WATER TEMP (^{O}C)		
pH		
SP. CONDUCTIVITY (us/cm)		
DO (mg/L)		
TURBIDITY (NTU) (degree of clarity if no probe)		
SPMD EXPOSURE		
TOTAL TIME (min/sec)		
NOTABLES (e.g., contamination, damage, tins dented, rain/blowing snow etc.)		
FILM PHOTOS	N/A	☐ yes ☐ no
BIOFOULING CLASS BF = biofilm SS = suspended sediment	N/A ☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 **Classes** **0**- No apparent BF/SS **1** - Slight BF/SS (slight discoloration and/or reduction in transparency). **2**- Low BF/SS (visible and patchy growth/accumulation of BF/SS). **3**- Moderate (film surface evenly covered by thin growth/accumulation of BF/SS). **4**- High BF/SS (film surface obscured by thick growth/accumulation of BF/SS).	

BED SEDIMENT EXPOSURE CLASS BS = bed sediment	Dominant Substrate on Deployment: ☐ < 2cm sediment ☐ > 2cm sediment ☐ silt/clay ☐ sand ☐ gravel ☐ cobble ☐ armoured	☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 **0**- No BS apparent **1**- <1/4 surface area covered by BS. **2**- 1/4 to 1/2 surface area covered by BS **3**- 1/2 to 3/4 surface area covered by BS **4**- > 3/4 surface area covered by BS

Appendix D. Field Audit Checklist

SPMD FIELD AUDIT

FIELD AUDIT DATE:
AUDITOR NAME:
SITE NAME:
CREW:

FIELD SHEETS					
All fields completed:	Y (Yes) N (No)	If N (No) - Describe	Follow-Up Actions / Responsible authority	Follow-Up By: Date	Outcome / Date
sampling event details					
site drawing					
weather conditions					
other samples					
site and flow conditions					
field measurements					
spmd exposure					
EQUIPMENT					
Equipment Box is complete:	Y (Yes) N (No)	If N (No) - Describe	Follow-Up Actions / Responsible authority	Follow-Up By: Date	Outcome / Date
all tools necessary are available					
SPMDs include appropriate:	Y (Yes) N (No)	If N (No) - Describe	Follow-Up Actions / Responsible authority	Follow-Up By: Date	Outcome / Date

samples (standard and experimental)					
field blanks					
trip blanks (if required)					
same lot numbers					
appropriate labelling (sample type, date, location)					
clean canister					
Coolers contain:					
ice					
hobos					
YSI is:					
calibrated					
PROCEDURES					
SOPs are adhered to:	Y (Yes) N (No)	If N (No) - Describe	Follow-Up Actions / Responsible authority	Follow-Up By: Date	Outcome / Date
sample and blank exposure to potential contaminants minimized (e.g., boat motor) and noted in field sheets					

samples and blanks are handled as per the SOP to minimize damage and contamination					
sample and field blank were exposed as per SOPs (e.g., synchronized exposure)					
sample and field blank exposure time was minimized while taking due care not to compromise the sample or health and safety					
clean canister was used for deployment					
deployment depth was approximately 1m from the surface (except in shallow waters) and SPMDs do not contact the bed					
field sheet and films were photographed upon retrieval					
tins were sealed and seal checked					
temperature logger was retrieved/deployed					

Additional information can be obtained at:

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200 Sacré-Coeur Boulevard
Gatineau QC K1A 0H3
Telephone: 1-800-668-6767 (in Canada only) or 819-997-2800
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