

6.13 PROTOCOL FOR TRACE ORGANIC CONTAMINANTS AND PESTICIDES SAMPLING

Overview

Trace organic sampling use grab or composite sampling techniques as long as consideration is given to the following points.

- Only glass, Teflon, or stainless steel that are cleaned to trace organic standards, should be in contact the sample.
- Samples should not have any headspace and should be collected in amber or dark glass bottles to limit potential photo-degradation.
- Minimize sample aeration to limit volatilization.
- Avoid using an intermediate container to fill samples bottles (a contamination concern).
- Preserve samples as required by the laboratory.
- When sampling under ice, some vials used for volatile priority pollutants (VPP) are difficult to fill. Ensure the auger hole is well flushed and lower the vials by hand as deep as possible, then cap below the surface. Alternately, a clean trace organic 1L brown bottle can be filled and VPP vials immediately poured off from the 1L brown bottle ensuring no head space.

For blanks, use ultra-pure de-ionized water (highest-grade de-ionized water used in the analysis of the trace organic parameters being sampled) supplied by the appropriate analytical laboratory section for field blanks.

Sources

Alberta Environment (2006 a), Environment Canada (2006 b), Environment Canada (1999)

At a glance

- 1** Do not rinse bottles (unless instructed to by the laboratory) and do not touch the inside of the lid or mouth of the bottle.
- 2** Pesticide and AOX sample bottles may be filled from a 4 L polycarbonate bottle (Photo 13).
- 3** In rivers, submerge the bottle directly in the flow facing upstream. Cap below the surface once full. When sampling from a bridge, place bottle in stainless holder with foam insert, keep cap of bottle on until bottle is inserted in place. This avoids the risk of touching the bottle mouth to the stainless holder. Lower into main flow, raise bottle up and down in the flow until full, then carefully remove the holder to bridge level and cap the bottle. When sampling under ice, place bottle in stainless steel holder with foam insert and drop quickly into the main flow below the ice. Cap below the surface when full.
- 4** In lakes, either for open water or under ice, use a peristaltic pump to collect a vertically integrated composite, ensuring that

Teflon tubing is used. Submit a QA/QC pump equipment blank to check for possible contamination.

Large sample extraction

1 A benefit of in-field large sample extraction is the reduced detection limits. This is due to the larger sample (20 to 40 litres). Two types of samplers are the Goulden Large Sample Extractor and the Pressure Container sample extractor.

Pressure container sample extractor

The PCSE is a liquid-liquid large sample extractor, which uses dichloromethane (DCM) to concentrate hydrophobic trace organics. It is not a flow-through extractor, and may be thought of as a larger variation of the separatory funnel extraction technique used in most laboratories. The PCSE offers certain advantages over flow-through systems including simplicity and ease of operation.

1 Water samples are collected in pre-washed 20-litre stainless steel beverage containers. The samples are filtered under nitrogen pressure through in-line stainless steel holders (142 mm GF-C or AE) into Millipore stainless steel pressure containers for solvent extraction. Alternatively, centrifugate can be extracted, making the filtering step unnecessary.

2 A known volume of recovery standards (in methanol) are added to the pressure container.

*extract in
two stages*

3 Samples are extracted in two stages. An initial volume of 600 mL DCM is added to the pressure container, stirred at slow speed with a stainless steel and Teflon mechanical stirrer for 15 minutes. The DCM is then allowed to settle to the bottom for 15 minutes and forced under low nitrogen pressure into a sample container. Any residual water entering the sample container is poured back into the pressure container.

4 A second aliquot (300 mL) of DCM is added to the pressure container, stirred for 15 minutes, and allowed to settle for 15 minutes. The second stage extract is then combined with the first stage extract to complete the sample.

5 At this point, the pH of the sample can be adjusted and the procedure repeated to extract acid or base extractable compounds. The required time for extraction of a 20-litre PCSE sample, including cleanup, is approximately 2 hours.

Goulden large sample extractor

1 The sampler and all Teflon tubing are cleaned between surveys using organic-free cleaning protocols including detergent washing, organic-free de-ionized water rinses, acetone then hexane rinses, followed by air drying. Between samples

during surveys, the sampler is rinsed with acetone, hexane, and organic free water between sites, with all glassware openings covered with fired aluminum foil (fired aluminum foil: place aluminum foil in muffle furnace for 3-6 hours at 400°C) when not in use. If possible, surveys are designed to move from sites of lower probable contaminants to higher contaminants to reduce the possibility of cross-contamination.

2 Samples are collected in pre-cleaned 4-litre glass containers or 20-litre stainless steel beverage pressure containers (all rubber o-rings on the beverage container should be replaced with vitex o-rings). The sample is filtered before extraction to reduce dichloromethane (DCM) emulsion, which can lead to reduced extraction recovery. Filtering can be accomplished by using a Millipore 142 mm stainless steel in-line filter holder and GF-C paper under nitrogen pressure (using a beverage pressure container). The filter paper should be retained (wrap in fired aluminum foil, then in a Ziploc-type bag) for subsequent laboratory extraction. The water and sediment extracts are subsequently combined to provide a result for whole water. An alternative to filtering is to extract centrifugate in the sampler and analyze suspended sediments from the sedi-sampler.

3 An initial volume of 300 mL DCM (pesticide grade) is added to the mixing chamber, and sample water pumped into the sampler through glass and Teflon tubing at a rate of 500 mL/minute. The sample is heated by a core heater to approximately 20° C to increase extraction efficiency, and mixed by a stainless steel mechanical stirrer. A second pump adds a precise volume of recovery standards (in methanol) to the mixture throughout the extraction process. A third pump replaces DCM, which is lost due to water solubility (1.6%). The pumps and mixer should be stopped periodically during the process to ensure that the DCM level remains near the original 300 mL mark. If the DCM level varies, the makeup rate should be adjusted. The standard should be added until approximately 10 minutes before the end of the extraction process to allow time to rinse the standard container and purge the intake line with an additional volume of analytical grade methanol.

4 Following extraction, the DCM extract is decanted to 1-litre pre-cleaned amber glass containers using a Teflon separatory funnel (to reduce emulsion). Repeated rinsing of the sampler with extracted water is generally required to remove entrapped DCM, particularly from the packed Teflon column. Any solvent that reaches the third stage settling chamber is added to the extract. DCM lot numbers should be recorded and solvent blanks and method blanks (using organic free water spiked with recovery standards) should be collected at pre-planned intervals. The time required for extraction of a 40-litre sample averages

approximately 2.5 hours, allowing time for extraction, sample recovery, and cleanup.

**Other
sources**

ISO 2008 (b), Environment Canada Undated (a), Personal Com
M. Sekela, Environment Canada (2009)

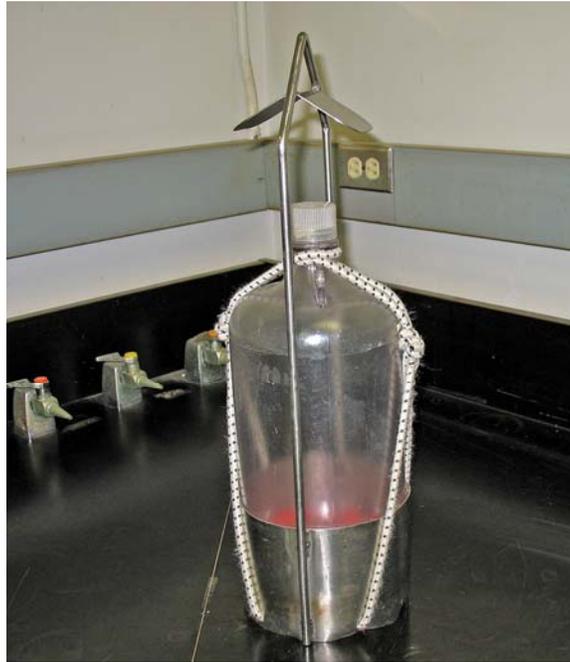


Photo 13: Example of a 4-litre sampler
(Courtesy: Darcy McDonald, Alberta
Environment)