Appendix 2. Chemical Analysis of Water, Sediment, and Fish

Contents

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Water, bottom-sediment, fish-tissue, stormwater, and passive in situ chemical-extraction samples were analyzed for 209 PCB congeners using high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS). Fish-tissue samples were also analyzed for three nonorthosubstituted, coplanar PCBs using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).[15]

PCB–Congener Analysis

AXYS Analytical Services, Ltd., a commercial laboratory in Sidney, British Columbia, Canada, analyzed the water, bottom-sediment, and fish-tissue samples. Methods were documented in internal documents prepared by AXYS Analytical Services, Ltd., hereafter named AXYS Analytical (AXYS Analytical, written commun., 2005). The condition of each sample received at the laboratory was noted, including labeling, holding times, and temperature. Samples were stored at the laboratory at -20°C until analysis. Just prior to analysis, samples or subsamples split on the basis of weight were spiked with a blend of isotopically labeled (^{13}C) surrogate standards and extracted. Sediment and tissue samples were dried with sodium sulphate (Na_2SO_4) prior to extraction. Samples were extracted by means of the Soxhlet procedure with dichloromethane (DCM), with the exception of particulate samples, which were extracted by the Dean-Stark procedure with toluene. Tissue samples were also eluted through a gel-permeation column to remove lipids. For water samples, the masses of PCBs on the filter and resin column (in nanograms) quantified the mass of PCBs in the volume of water that had passed through the filter and column in each sample. Mass values were divided by the volume of each water sample to give dissolved and particulate PCB concentrations. Teflon sample bags used to collect water samples were rinsed with seastar water, methanol, and DCM, in that order. After the methanol and water were discarded, the DCM was dried by means of Na_2SO_4 and added to the XAD extract.

Next, extracts were split into two or more samples by weight; one split sample was archived or, in the case of tissue analysis, used for HRGC/HRMS. The one-half of the extract for chemical analysis was purified by means of Florisil or a combination of Florisil, acid/base silica, and alumina chromatographic columns (not necessarily in that order). Tissue-sample extracts were further purified in carbon celite chromatographic columns to remove selected analytes. Once purified, the extracts were reduced in volume, spiked with labeled recovery (internal) standards, and split into two equal fractions. One fraction was analyzed for PCBs by HRGC/LRMS. In some cases, extracts were diluted and reanalyzed.

PCB concentrations were determined by HRGC/LRMS with a gas chromatograph (GC) equipped with a quadrupole mass spectrometer (MS). A J&W Scientific, Inc., DB-5 chromatography column (60 m, 0.25-mm inside diameter, 0.10-µm film thickness) was coupled directly to the MS source. The MS was operated at a unit-mass resolution in the electron ionization (EI) mode with multiple ion detection (MID) that acquired two characteristic ions for each target analyte and surrogate standard. A splitless/split injection sequence was used (AXYS Analytical, written commun., 2005). Gas chromatography/electron capture detection (ECD) analysis was done with a gas chromatograph, a ^{63}Ni electron-capture detector, and an integrator. A J&W Scientific DB–5 capillary column was coupled directly to the ECD source. When needed, confirmation was provided by simultaneous analysis with a J&W Scientific DB–17MS capillary column (30 m long, 0.25-mm inside diameter, 0.25-µm film thickness) (AXYS Analytical, written commun., 2005).

Coplanar PCB congeners were analyzed by means of a Micromass Ultima high-resolution mass selective detector (MSD) interfaced to a HP 6890 GC. A DB–5 chromatography column was coupled directly to the MS source. The MS was operated at 10,000 (static) mass resolution in the EI mode with MID. At least two ions were acquired for each target and surrogate compound. Target concentrations were determined by the isotope-dilution or internal-standard method by means of Micromass OPUSQUAN software. A splitless/split injection sequence was used.

Initial calibration was done by means of a series of solutions that covered the working concentration range of the instrument. These solutions contained surrogates, recovery standards, and target compounds. Calibration was verified at least once every 12 hours by analysis of a midlevel calibration standard. Sample-specific detection limits were determined from the analysis data by converting the minimum detectable signal (equal to three times the noise level) to a concentration by the same procedures used to convert the target peak response to concentrations. (AXYS Analytical, written commun., 2005).

Bias and Variability of PCB–Congener Concentrations

Environmental samples were analyzed by AXYS Analytical in batches of 20 samples or fewer. Each sample batch was accompanied by quality assurance/quality control (QA/QC) samples—including procedural blanks, ^{13}C-labeled surrogate standards, labeled recovery (internal) standards, matrix-spike samples, or laboratory duplicate samples—to test laboratory bias and variability. Before analytical results were accepted, QA/QC had to meet method criteria that included PCB–congener concentrations measured in procedural blanks that were less than 1 ng/sample; congener-specific percent-recovery values for ^{13}C-labeled surrogate standards, recovery standards, and matrix-spike samples that generally were 40–130 percent, 60–130 percent, and 60–130 percent, respectively; and relative percent differences (RPD) between duplicate samples of 40 percent or less. Laboratory instruments were calibrated in

[15] Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

accordance with AXYS Analytical's standard operating procedures (SOP; AXYS Analytical, written commun., 2005). The percent difference between midlevel calibration standards and calibration verification concentrations had to be within 20 percent of the actual concentrations. The condition of each batch and the results of QA/QC samples are discussed by sample type and batch in appendix 3.

Elemental Analysis

SGS Laboratory, a commercial laboratory in Ontario, Canada, analyzed the bottom-sediment samples. The condition of each sample received at the laboratory was noted, including labeling, holding times, temperature. Just prior to chemical analysis, an aliquot (about 1 g) was collected from each bottom-sediment grab sample and milled in a stainless-steel mortar.[16] Next, the sample was digested in 2 mL of nitric acid HNO_3 and heated at 80 to 90°C for 0.5 hour. After the sample had cooled slightly, the digestates were spiked with 4 mL of hydrochloric acid (HCl) and heated for 2 hours in a water bath. Next, the digestates were allowed to cool to room temperature and diluted with distilled water to a final volume of 20 mL. About 5 mL of this solution was poured into a test tube for inductively coupled plasma mass spectrometry (ICP–MS) analysis by an Optima spectrometer.

[16] Milling of bottom-sediment samples may expose to the digestive acids elements that otherwise would be locked in mineral grains. Therefore, elements exposed to digestive acids by milling are likely to be detected at greater concentrations than elements in unmilled samples. Milling may bias samples by increasing measured concentrations of chromium and nickel.

Bias and Variability of Element Concentrations

Environmental samples were analyzed by SGS in batches of up to 40 samples. Each batch was accompanied by QA/QC samples—including procedural blanks, laboratory spikes, matrix spikes, matrix-spike samples, recovery standards, or standard reference material—to test laboratory bias and variability. Before analytical results were accepted, QA/QC samples had to meet method criteria that included element concentrations measured in procedural blanks that were less than quantification limits; RPDs between laboratory duplicate and matrix-spike samples that were no more than 10 percent; percent-recovery ranges that were 50–100 percent; and standard reference materials that were within 20 percent of certified values. Laboratory instruments were calibrated in accordance with the SOPs of SGS (SOP; SGS, written commun., 2005) and were required to meet method specifications. The condition of each batch and the results of the QA/QC analysis are discussed by sample type and batch in appendix 3.

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