Appendix 3. Quality Assurance and Quality Control

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Field and laboratory quality-assurance/quality-control (QA/QC) samples were evaluated as part of this study. Field QA/QC samples included field duplicates, ^{13}C-labeled field spikes, an equipment blank, a standard reference material, and a pair of samples collected to characterize differences between fixed-point samples and samples integrated across the channel cross section. Laboratory QA/QC samples included procedural blanks, ^{13}C-labeled surrogate standards, recovery standards, matrix-spike samples, and laboratory duplicate samples.

Bias and Variability in Field and Laboratory Analyses

Environmental samples were collected and analyzed along with QA/QC samples, including field duplicates and ^{13}C-labeled field spikes. These QA/QC samples were collected, processed, and analyzed in exactly the same way as the environmental samples. Therefore, by their very nature, field QA/QC samples are affected by bias and variability associated with environmental conditions, sample collection, and sample processing, as well as with laboratory processing (appendix 1). Duplicate PISCES samples were collected at 7 of 15 locations from two samplers hung from the same buoy/cinder block at the same location and analyzed separately. Duplicate sediment samples collected at 2 of 13 locations consisted of two representative aliquots of sediment that were taken from separate bottom-sediment grab samples and analyzed separately. Field spikes were processed by XAD columns that were spiked with ^{13}C-labeled surrogate standards.

Field QA/QC data[17] indicate that PCBs (and other constituents) in samples were neither lost nor gained as a result of processing, shipping, handling, holding times, or laboratory analytical procedures:

- RPDs for total PCB-congener concentrations between duplicate PISCES samples ranged from 0.56 to 69 percent and averaged about 32 percent; however, the range of RPDs for individual PCB congeners was much wider;
- RPDs for total PCB-congener concentrations between duplicate sediment grab samples ranged from 26 to 51 percent and averaged about 39 percent; however, the range of RPDs for individual PCB congeners was much wider;
- Root mean square differences (RMSDs) between PCB concentrations in duplicate PISCES samples ranged from 0.05 to 0.30 and averaged about 0.18;
- RMSDs between PCB concentrations in duplicate sediment grab split samples ranged from 0.11 to 0.21 and averaged about 0.16;
- RPDs calculated for detectable element concentrations between duplicate bottom-sediment grab samples were less than 25 percent (8.9 percent, on average) with a few exceptions. In particular, RPDs calculated for detectable copper, molybdenum, silver, and zinc concentrations measured in BGY–141 split samples were 26, 46, 86, and 27 percent, respectively; and
- Percent recoveries of ^{13}C-labeled surrogate standards measured in spiked XAD columns ranged from 82 to 130 percent and averaged about 100 percent (table 3–1).

In addition to routine QA/QC, samples were collected to test the study design. Specifically, the use of a single point sample to represent concentrations across the river was tested by collecting paired water samples. The sample pair consisted of a 17–L water sample collected at the fixed-point sampling location (the USGS streamgage at Milton Village) by means of the pump from the automatic sampler and a 14–L water sample collected by equal-width increment (EWI) methods (Wilde and others, 1999) at the same time from the entire width of the river. These samples were processed and analyzed by the same methods as the other water samples.

Table 3–1. Percent recoveries of ^{13}C-labeled surrogate standards measured in spiked XAD columns.

[^{13}C, Carbon-13, a natural, stable isotope of carbon; EWI, equal-width-intergrated sample; --, not done]

Sample	Batch	^{13}C-labeled surrogates		
		PCB-31	PCB-95	PCB-153
May 05a	WG16542	93.3	103	96.7
May 05b	WG16542	100	99.4	103
June 05	WG16542	94.3	107.0	107
July 05	WG16542	102	112	108
August 05	WG16542	130	116	107
September 05	WG17610	82.5	97.7	102
October 05	WG18055	103	89.4	93.3
November 05	WG18055	103	89.4	93.3
December 05	WG18692	--	--	--
January 06	WG18692	--	--	--
February 06	WG18692	--	--	--
March–April 06	WG18692	--	--	--
Point sample	WG18692	--	--	--
EWI	WG18692	--	--	--
Blue Hill Avenue	WG17610	86.0	97.5	95.5
Central Avenue	WG17610	87.1	98.4	102
Tap water	WG17610	85.1	103	104

[17] Data presented here are from PISCES and sediment-grab samples collected as part of this study.

Comparison of calculated PCB-congener concentrations[18] measured in fixed-point and EWI samples indicates that, at least under the flow conditions at the time of sampling, concentrations measured through fixed-point sampling could be considered representative of the entire cross section; RPDs were about 18 percent, on average, for all PCB congeners (table 3–2). More than 90 percent of the detected PCB-congener concentrations were greater in the EWI sample than in the fixed-point sample; however, the RPDs between the EWI and fixed-point samples were low with a maximum of about 43 percent. Some of the observed differences between the concentrations measured in the EWI and fixed-point samples may be explained by environmental variability. The fixed-point sample was collected during a time interval of about 5 minutes, whereas the EWI sample took about 45 minutes to collect; during this time interval, the flow increased from 1,680 to 1,750 ft^3/sec. PCB-congener patterns measured in fixed-point and EWI samples were also similar with an RMSD equal to 0.41.

Because about 1 L of tap water was used to rinse sample bags and equipment, it was necessary to ensure that the tap water was free of PCBs, or at least to quantify tap-water PCB concentrations and thus to determine the effectiveness of cleaning. Some tap water that had been used to rinse a sample bag was collected as an equipment blank sample. Several individual PCB congeners were detected in the tap-water equipment blank; however, most did not meet AXYS Analytical quantification limits (table 2–3). Of the PCB congeners that were measured at concentrations greater than analytical quantification limits, only one group of unresolved PCB congeners (PCB 47 + 48 + 75) was detected in particulate (1.06 ng/sample) and dissolved (4.56 ng/sample) form at concentrations above 1 ng/sample (considered acceptable for blank samples). PCB 6 (0.104 ng/sample), PCB 14 (0.122 ng/sample), PCB 51 (0.582 ng/sample), and PCB 89 + 90 + 101 (0.112 ng/sample) were detected in the XAD sample, but the concentrations were all less than 1 ng/sample. The total concentrations of PCB-congeners measured in particulate and dissolved tap-water samples corresponded to a particulate PCB concentration of about 0.063 ng/L and a dissolved PCB concentration of about 0.324 ng/L. It is unclear whether or not PCBs in the equipment blank were the result of contaminated tap water or inadequate cleaning of filter apparatus.

XAD columns with sufficient sorptive capacity were used to sorb dissolved PCBs in large-volume (about 20-L) water samples collected from the Neponset River. The sorptive capacity needed was determined from PCB-congener concentrations measured in samples collected in PISCES samplers deployed near the USGS Milton Village streamgage in the Walter Baker Impoundment (Breault and others, 2004a). The ability of XAD resin to sorb PCBs was tested by filtering an environmental sample through two XAD columns in series; breakthrough of PCBs would be indicated by the detection of PCBs on the second column. Only one group of unresolved PCB congeners (PCB 47 + 48 + 75) was detected in the second XAD column (0.621 ng/sample, less than 0.4 percent of the total dissolved PCB concentration for that sample).

[18] PCB-congener concentrations (ng/L) were calculated by dividing the mass of PCB congeners measured in water samples (ng/sample) by the volume of water filtered (L). Estimated congener concentrations and censored congeners were excluded.

Flow-Proportional Water Samples (AXYS Batches WG16542, WG17610, WG18055, and WG18692)

On July 19, August 1, and September 13, 2005, XAD columns, GFFs, and Teflon bags were shipped overnight from U.S. Geological Survey (USGS) in Northborough, MA, to AXYS Analytical Services, Ltd. in Sidney, British Columbia (hereafter named AXYS Analytical, Ltd.). Columns, GFFs, and Teflon bags were shipped in coolers packed with ice. The condition of the columns, glass-fiber filers (GFFs), and Teflon sample bags received by the laboratory was good. Although temperatures in the coolers were high (16 to 27°C), AXYS Analytical scientists determined that these high temperatures would not compromise the integrity of the samples (Brian Fowler, AXYS Analytical, Sidney, British Columbia, written commun., 2005). The samples were assigned batch number WG16542. PCB-congener concentrations measured in the blank sample analyzed with batch WG16542 were all less than the detection limit. The percent surrogate recoveries of the ^{13}C-labeled PCB 3, PCB 28, PCB 101, PCB 118, PCB 180, PCB 202, and PCB 206 surrogates were below method criteria in the XAD procedural blank; however, it was determined that this difference would not substantially affect PCB-congener quantification (Candice Navaroli, AXYS Analytical, Sidney, British Columbia, written commun., 2005). The percent recoveries of PCB 37 (133 percent) and PCB-54 (56.4 percent) in particulate XAD matrix-spike samples were above and below method criteria, respectively. As a result, PCB 37 and PCB 54 data for batch WG16542 were flagged as outside quantification limits and excluded from data analysis. All other QA/QC results were within method criteria. No laboratory duplicates were analyzed with this batch.

On November 9, 2005, XAD-2 columns, GFFs, and Teflon bags were shipped to AXYS Analytical. The condition of the columns, GFFs, and Teflon sample bags received by the laboratory was good. These samples were assigned batch number WG17610. Two blank samples (WG17610-101 and WG17610-103) were analyzed with batch WG17610. Most PCB-congener concentrations measured in blank sample WG17610-101 were less than the detection limit; however, 26 PCB congeners were detected. Of these, the concentration of only one PCB congener (PCB 36; 1.06 ng/sample) was greater than 1.0 ng/sample. Similarly, most PCB-congener concentrations measured in the other blank sample (WG17610-103) were less than the detection limit; however, 16 PCB congeners were detected. Of these, the concentration of one PCB congener (PCB 7; 1.52 ng/sample) was greater than 1.0 ng/sample. The percent recoveries of the ^{13}C-labeled PCB 3, PCB 8, and PCB 28 surrogates in the XAD procedural blank and the ^{13}C-labeled PCB-3 surrogate in water samples collected at Blue Hill Avenue and Central Street were below method criteria; however, it was determined that this difference would not substantially affect PCB-congener quantification (Ziqing Ou, AXYS Analytical, Sidney, British Columbia, written commun., 2005). The percent recoveries for matrix spikes were within method criteria for all PCB congeners with the exception of particulate concentrations for PCB 54 measured in a spiked XAD-2 column (63.5 percent); percent recoveries may be similar for PCB 54 measured in environmental samples. No laboratory duplicates were analyzed with this batch.

On December 14, 2005, XAD-2 columns, GFFs, and Teflon bags were shipped overnight to AXYS Analytical. The condition of the columns, GFFs, and Teflon sample bags received by the laboratory was good. These samples were assigned batch number WG18055. PCB-congener concentrations measured in the blank sample analyzed with batch WG18055 were all less than the detection limit, with two exceptions: PCB 7 (0.586 ng/sample) and PCB 11 (0.394 ng/sample), were detected but in concentrations less than 1.0 ng/sample. Percent recoveries for ^{13}C-labeled surrogate standards and labeled recovery (internal) standards were within method criteria. The percent recoveries for particulate matrix spikes were within method criteria for all PCB congeners with the exception of PCB 54 (63.5 percent) measured in a spiked XAD-2 column and GFF; percent recoveries may be similar for PCB 54 measured in environmental samples. No laboratory duplicates were analyzed with this batch.

On February 21, March 15, May 16, and June 14, 2006, XAD-2 columns, GFFs, and Teflon bags were shipped overnight to AXYS Analytical. The condition of the columns, GFFs, and Teflon sample bags received by the laboratory was good, with one exception: samples shipped on March 15, 2006 arrived at the laboratory at 6°C, slightly higher than the targeted temperature (4°C). These samples were assigned batch number WG18692. Two blanks were analyzed along with batch WG18692. A few PCB congeners were measured in the first blank sample analyzed with batch WG18692, but all detected PCB-congener concentrations were less than 1.0 ng/sample. No PCB congeners were detected in the second blank sample analyzed with batch WG18692. The percent recoveries of ^{13}C-labeled surrogate standards and labeled recovery (internal) standards were within method criteria, with one exception. The percent recoveries of the ^{13}C-labeled PCB 28, PCB 101, PCB 118, PCB 180, PCB 202, PCB 206, and PCB 209 surrogates in particulate samples collected during February 2006 were below method criteria. Matrix-spike percent recoveries were within method criteria for all PCB congeners. No laboratory duplicates were analyzed with this batch.

Passive In Situ Chemical-Extraction Samples (AXYS Batches WG13865 and WG16781)

On September 2, 2004, four hexane samples collected from passive in situ chemical extraction samplers (PISCES) were shipped overnight in a cooler packed with ice to AXYS Analytical. The condition of the hexane samples received by the laboratory was good. These samples were assigned batch number WG13865. PCB-congener concentrations measured in the blank sample analyzed with batch WG13865 were all less than the detection limit. Percent recoveries for ^{13}C-labeled surrogate standards, labeled recovery (internal) standards, and matrix-spike samples were within method criteria, with one exception: the percent surrogate recoveries of ^{13}C-labeled surrogates in the procedural blank were all below method criteria because some of the blank sample was accidentally spilled in the laboratory. It is unlikely that this accident affected the analytical results (Ziqing Ou, AXYS Analytical, Sidney, British Columbia, written commun., 2005). No laboratory duplicates were analyzed with this batch.

On August 16, 2005, 18 hexane samples collected from PISCES samplers were shipped in a cooler packed with ice overnight to AXYS Analytical. The condition of the hexane samples received by the laboratory was good; however, the temperature in the cooler (6°C) was slightly higher than the targeted temperature (4°C). These samples were assigned batch number WG16781. PCB-congener concentrations measured in the blank sample analyzed with batch WG16781 were all less than the detection limit, with three exceptions: PCB 105 + 127 (0.916 ng/sample), PCB 179 (1.51 ng/sample), and PCB 206 (0.268 ng/sample). As a result of these findings, PCB 179 data were flagged as outside quantification limits and excluded from data analysis. Percent recoveries for ^{13}C-labeled surrogate standards, labeled recovery (internal) standards, and matrix-spike samples were within method criteria. No laboratory duplicates were analyzed with this batch.

Bottom-Sediment Grab Samples (AXYS Batch WG16492)

On June 7, 2005, 14 bottom-sediment grab samples were shipped overnight in a cooler packed with ice to AXYS Analytical. The condition of the grab samples received by the laboratory was good; however, the temperature in the cooler (10°C) was slightly higher than the targeted temperature (4°C). These samples were assigned batch number WG16492. PCB-congener concentrations measured in the blank sample analyzed with batch WG16492 were all less than the detection limit, with two exceptions: PCB 137 (0.024 ng/sample) and PCB 209 (0.023 ng/sample), which were detected but in concentrations less than 1.0 ng/sample. The percent recoveries for ^{13}C-labeled surrogate standards, labeled recovery (internal) standards, and matrix-spike samples were within method criteria. Bottom-sediment grab sample QYY 003, which was collected from the Neponset River Estuary, was selected by laboratory personnel for duplicate analysis. The RPDs for PCB-congener concentrations between duplicate aliquots of sample QYY 003 were less than 40 percent and averaged 8 percent.

Fish-Tissue Samples (AXYS Batches WG15112, WG17077, WG17812, and WG19863)

On September 2, 2004, 16 white sucker were shipped overnight to AXYS Analytical. Fish were wrapped in hexane-rinsed aluminum foil and packed in a cooler with ice. The condition of the tissue samples received by the laboratory was good. These fish were skinned, filleted, and assigned batch number WG15112. PCB-congener concentrations measured in the blank sample analyzed with batch WG15112 were all less than the detection limit. The percent recoveries for ^{13}C-labeled surrogate standards, labeled recovery (internal) standards, and matrix-spike samples were within method criteria. No laboratory duplicates were analyzed with this batch.

Skinless fillet extracts, which were analyzed for coplanar PCB congeners by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), were also assigned batch number WG15112. PCB-congener concentrations measured in the blank sample (corn oil) analyzed with batch WG17077 were detected at very low levels (PCB 77, 0.00045 ng/sample; PCB 126,

0.00051 ng/sample; and PCB 169, 0.00053 ng/sample). The percent recoveries of ^{13}C-labeled surrogates and matrix-spike samples were within method criteria. No laboratory duplicates were analyzed with this batch.

On September 26, 2005, 16 whole white sucker were shipped overnight to AXYS Analytical. The fish were wrapped in hexane-rinsed aluminum foil and packed in a cooler with ice. The condition of the tissue samples received by the laboratory was good. These samples were assigned batch number WG17812. PCB-congener concentrations measured in the blank sample analyzed with batch WG17812 were all less than the detection limit, with one exception: PCB 7 (0.327 ng/sample), which was detected at a concentration less than 1.0 ng/sample. The percent recoveries of ^{13}C-labeled surrogates in the fish-tissue sample collected from the Tileston and Hollingsworth Impoundment were generally within the method criteria; however, PCB 118 (131 percent), PCB 180 (130 percent), and PCB 202 (130 percent) were high. Generally, the percent recoveries for matrix-spike samples were also within the method criteria; however, PCB 43 + 49 (68.3 percent), PCB 52 + 73 (69.2 percent), and PCB 54 (63.3 percent) were low. No laboratory duplicates were analyzed with this batch.

Whole fish-tissue extracts, which were analyzed for coplanar PCB congeners by HRGC/HRMS, were assigned batch number WG17077. PCB-congener concentrations in the blank sample (corn oil) analyzed with batch WG17077 were detected at very low levels (PCB 77, 0.00170 ng/sample; PCB 126, 0.00054 ng/sample; and PCB 169, 0.00061 ng/sample). The percent recoveries for ^{13}C-labeled surrogates and matrix-spike samples were within method criteria. No laboratory duplicates were analyzed with this batch.

On July 6, 2006, 21 whole common mummichog were shipped overnight to AXYS Analytical. Fish were wrapped in hexane-rinsed aluminum foil and packed in a cooler with ice. The condition of the tissue samples received by the laboratory was good. These samples were assigned batch number WG19863. PCB-congener concentrations in the blank sample analyzed with batch WG19863 were all less than the detection limit. The percent recoveries for ^{13}C-labeled surrogate standards, labeled recovery (internal) standards, and matrix-spike samples were within method criteria. No laboratory duplicates were analyzed with this batch.

Whole fish-tissue extracts, which were analyzed for coplanar PCB congeners by HRGC/HRMS, were also assigned batch number WG19863. PCB-congener concentrations measured in the blank sample (corn oil) were detected at very low levels (PCB 77, 0.000482 ng/sample; PCB 126, 0.000272 ng/sample; and PCB 169, 0.000248 ng/sample). The percent recoveries of ^{13}C-labeled surrogates and matrix-spike samples were within method criteria. No laboratory duplicates were analyzed with this batch.

Bottom-Sediment Grab Samples (SGS, Batch 084037)

On August 7, 2005, 14 bottom-sediment grab samples were shipped overnight to SGS, Toronto, Ontario. Bottom-sediment grab samples were shipped in a cooler packed with ice. The condition of the grab samples received by the laboratory was good. These samples were assigned batch number 084037. Element concentrations measured in the blank sample analyzed with batch 084037 were all less than the detection limit. Bottom-sediment grab samples DDY–001 and QYY–003, which were collected from Mother Brook and the Neponset River Estuary, respectively, were selected by laboratory personnel for duplicate analysis. The RPDs for element concentrations between duplicate aliquots of samples DDY–001 and QYY–003 were less than 10 percent, with a few exceptions: the RPDs for beryllium concentrations between duplicate aliquots of sample DYY–001 and silver concentrations between duplicate aliquots of sample QYY–003 were about 40 percent. Element concentrations measured in performance and blind (standard submitted by USGS) performance standards were generally within acceptable limits; however, concentrations of 9 of the 23 elements measured in the blind performance sample were slightly higher than best estimates for the true number. Best estimates do not meet the National Institute of Standards and Technology (NIST) qualification limits; however, chemical concentrations are not certified in NIST standards if analyzed by means of a mild digestion like the one used as part of this study. NIST standards that were sent to SGS and analyzed by the same basic methods but with a more robust digestion (by hydrofluoric acid) generally were within certified values (Breault, R.F., U.S. Geological Survey, unpub. data, 2005).

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