APPENDIX M
OVERVIEW OF UPDATED BIAS CORRECTION

APPENDIX M
OVERVIEW OF UPDATED BIAS CORRECTION

Hudson River water column polychlorinated biphenyl (PCB) concentrations measured by General Electric (GE) in 1993 using the Green Bay Method (mGBM) compared with those measured as part of U.S. Environmental Protection Agency (EPA) RI/FS Phase II Study using a dual capillary column method, suggested that an analytical bias existed between the two datasets (Hydroqual 1997). Part of the bias was attributed to an error in the original calibration of the PCB standard used by GE for DB-1 analyses which was subsequently corrected (EPA 1987, 1994). The other cause of the bias is related to the analytical methods. The mGBM utilizes a DB-1 chromatographic column which separates PCBs into 112 chromatographic peaks, several of which contain multiple congeners. The dual column method used by EPA separates more congeners into separate peaks, resulting in fewer peaks containing multiple congeners. Coelution of congeners with differing response factors causes mass estimates to be sensitive to the assumption made regarding the relative amounts of the congeners that coelute in a single peak (Hydroqual 1997).

Investigations indicated that the assumption of the relative amounts of the congeners that coelute in DB-1 column peaks 5, 8, and 14 was the primary cause of the differences between the methods. As shown in Table M-1, these peaks each contain two PCB congeners, both di-chlorinated, except for peak 14 which contains a di- and a tri-chlorinated congener.

The correct quantitation of these congeners is particularly important because, for example, peak 5 can constitute > 70% of the Total PCB mass in Hudson River water. The magnitude of the bias depends on differences between the coeluting peak's congener response factors (RFs). Correction factors were developed to eliminate the bias. The correction factors (CFs) need to be updated periodically because the relative abundance of coeluting congeners in peaks 5, 8, and 14 changes over time in the Hudson River System.

Each time bias CFs were developed, archived samples were analyzed using the mGBM and a dual column method using a C18 column that can individually resolve the PCB congeners that coelute in DB-1 peaks 5, 8, and 14. Regression analyses were performed to develop

single-peak CFs by relating DB-1 peak concentrations to the sum of concentrations of the individual congeners coeluting in that peak as quantified using the C18.

The CFs developed in 1997 were based on 16 archived extracts for water samples collected in 1996-1997 from Fort Edward, Thompson Island Dam and the Plunge Pool stations. The CFs developed in 2004 were based on 30 Hudson River Monitoring Program (HRMP) archived extracts for water samples collected in 2003 from the Boat Launch at the base of Bakers Falls, TID-PRW2, and Schuylerville stations. The 2009 study was conducted using recently archived extracts from samples collected during the Phase 1 Remedial Action Monitoring program (RAM) to assure sample concentrations are representative of current conditions during dredging in the Hudson River. The CFs are based on 30 RAM archived extracts from May and June 2009 selected from the following four stations: 1) Automated Lock 5 station; 2) Automated TID; 3) Manual at Stillwater; and 4) Automated at Waterford. In each case, the archived samples were selected to cover a range of Total PCB and DB-1 peaks 5, 8, and 14 concentrations. Table M-2 provides a summary of the CFs developed in 1997, 2004 and 2009. See Attachment 1 for a detailed description of the generation of these CFs.

The 2009 correction factors shown in Table M-2 were not applied by Northeast Analytical Labs (NEA) for their reporting of Phase 1 data, using instead the 2004 CFs. Where noted in GE's Phase 1 Evaluation, water column results for mGMB peaks 5, 8, and 14 were recalculated using the ratio of their respective 2009 to 2004 CFs and total PCB concentrations were recalculated. As the 2009 correction factors for all three peaks are greater than those developed in 2004, concentrations for congeners in peaks 5, 8, and 14 as well as the total PCB concentration are higher for a given sample using the 2009 CFs.

M.1 REFERENCES

EPA, 1994. *Memorandum from M.D. Mullin of the U.S. EPA Environmental Research Laboratory – Duluth, Large Lakes Research Station to G.* Frame of GE Corporate Research and Development dated 21 November 1994.

EPA, 1987. *Quality Assurance Plan: Green Bay Mass Balance Study. 1.* PCBs and Dieldrin. Great Lakes National Program Office (prepared by D.L. Swackhamer).

Hydroqual, 1997. Development *of Corrections for Analytical Biases in the 1991 – 1997 GE Hudson River PCB Database.* Prepared for General Electric Company Corporate Environmental Programs, Albany, NY. June 1997.

QEA/ESI, 2004. *Technical Memorandum.* Prepared for General Electric Company Corporate Environmental Programs, Albany, NY. March 2004.

TABLES

Table M-1
Congeners which Coelute in Peaks 5, 8, and 14 in the Green Bay Method

Peak	Congeners	Structure
5	4, 10	2-2;26
8	5, 8	23;2-4
14	15, 18	4-4; 25-2

Table M-2
Correction Factors Developed in 1997 and Updated in 2004 and 2009

Peak	1997 CFs	2004 CFs	2009 CFs	Ratio (2009 : 2004)
5	0.65	0.61	0.81	1.33
8	0.45	0.36	0.51	1.42
14	1.44	1.26	2.26	1.79

ATTACHMENT 1

ENVIRONMENTAL STANDARDS
Setting the Standards for Innovative Environmental Solutions

Technical Memo

To: Bob Gibson – General Electric Company

From: David Blye – Environmental Standards, Inc.
Meg Michell – Environmental Standards, Inc.

CC: Jim Rhea – Anchor QEA, LLC
John Connolly - Anchor QEA, LLC
Mark Larue – Anchor QEA, LLC

Date: September 11, 2009

Re: Evaluation of Modified Green Bay Method (mGBM) Coelution Bias Correction Factors

---

Background/Introduction

Past comparison of water column PCB concentrations in samples collected by the General Electric Company (GE) in 1993 with those measured as part of the U.S, Environmental Protection Agency (US EPA) RRI/FS Phase II Study revealed that the PCB concentrations calculated for chromatographic peaks that contain coeluting (i.e., multiple) PCB congeners on the DB-1 capillary column used as part of the modified Green Bay Method (mGBM) employed by GE were inaccurate in some cases (HydroQual 1997). Corrections for the DB-1 peaks affected most by this bias, DB-1 Peaks 5, 8, and 14, were originally developed in 1997. For water column samples analyzed by the mGBM, correction factors (CFs) of 0.65, 0.45, and 1.44 were applied to all existing results for Peaks 5, 8, and 14, respectively, in the Hudson River water column database in 1997, and were applied to all samples collected and analyzed by GE from 1997 to the beginning of the Baseline Monitoring Program (BMP) in 2004. In 2004, a study was conducted using archived extracts from the previous sampling year (i.e., 2003) to verify the

mGBM CFs using recent Hudson River water column PCB data and, as a result, the CFs for Peaks 5, 8, and 14 changed slightly to 0.61, 0.36, and 1.26, respectively (QEA/ESI 2004). The updated mGBM CFs were applied to all samples collected and analyzed by GE since the initiation of the BMP in 2004.

The objective of the study reported here was to verify and update, if necessary, the mGBM CFs by analysis of archived extracts from Hudson River water column samples collected during Phase 1 dredging operations.

Procedure to Verify and Update Correction Factors for mGBM DB-1 Peaks 5, 8, and 14

Extract Selection

This study was conducted using recently archived extracts from samples collected during the Phase 1 RAMP to assure sample concentrations are representative of current conditions during dredging in the Hudson River.

Thirty archived extracts of Hudson River Remedial Action Monitoring Program (RAMP) samples collected during May and June 2009 were selected to cover the range of detectable concentrations observed since dredging began on May 15, 2009. Extracts were selected from the following four RAMP sampling locations to cover the range of PCB composition observed during dredging: 1) the automated station at Lock 5; 2) the automated station at Thompson Island Dam 3) the manual station at Stillwater; and 4) the automated station at Waterford. These stations were chosen because these are the monitoring stations closest to the dredging operations. The specific samples from these stations were selected to span the range of concentrations observed at these locations since dredging operations began, on a total PCB basis as well as for DB-1 Peaks 5, 8, and 14. The selected samples were reviewed and approved for use in this study by the Agency on June 24, 2009 (via e-mail) prior to conducting

the study. PCB concentration data based on the mGBM analysis for sample extracts used in this study are included in Table 1.

Analytical Procedure

The 30 sample extracts were originally analyzed with a DB-1 gas chromatographic capillary column using the mGBM (NEA207_03_R01, Appendix 28 of the *Hudson River PCBs Site Phase 1 Remedial Action Monitoring Program Quality Assurance Project Plan*, May 2009). The current study utilized a CP-SIL5/C18 capillary column as was used in the previous coelution bias CF development (HydroQual 1997 and QEA/ESI 2004). The C18 column was chosen based on its ability to baseline-resolve lower molecular weight PCB congeners, including those coeluting in DB-1 Peaks 5, 8, and 14 (i.e., BZ #'s 4, 5, 8, 10, 15, and 18).

Discussion of Results

Regression Analysis for 2009 RAMP Analysis Data

Similar to the analyses performed in 1997 and 2004, regression analyses were performed to develop single peak CFs by relating DB-1 peak concentrations to the sum of the concentrations of the individual congeners coeluting in that peak as quantified using the C18 column. Regression analysis results for the selected 2009 samples are shown in Figure 1. The slope of the regression line represents the coelution bias CF for a given DB-1 peak. Correlation coefficients close to unity and small p-values (i.e., less than 3.7E-13) suggest that the regression slopes are statistically significant, while relatively small y-intercept values justify the use of regression line slopes to define the peak CFs. Further, the near unity correlation coefficients and small y-intercepts suggest that the coelution bias in these three peaks is systematic and independent of sample location, consistent with results observed in the previous

1997 and 2004 analyses. Based on these regression results, current coelution bias CFs for DB-1 Peaks 5, 8, and 14 are 0.81, 0.51, and 2.26, respectively (Figure 1).

Comparison between 1997, 2003, and 2009 correction factors

The CFs developed in 2003 differed only slightly from those developed in 1997 (QEA/ESI 2004). Figures 3 through 5 compare the regression analyses performed in 2003 and 2009 for DB-1 Peaks 5, 8, and 14, respectively. These regression results suggest that the correction factors developed in 2009 differ from those developed in 2009, particularly for DB-1 peaks 8 and 14.

The CF for peak 5 increases from 0.61 to 0.81 between the 2003 and 2009 regressions, which is a difference that is considered statistically significant because the 95% confidence intervals on the two regression lines do not overlap (Figure 2).

The CF for peak 8 increases from 0.36 to 0.51 between the 2003 and 2009 regressions; which is a difference that is considered statistically significant because the 95% confidence intervals on the two regression lines do not overlap (Figure 3).

The CF for peak 14 increased from 1.26 to 2.26, which is a difference that is considered statistically significant because the 95% confidence intervals on the two regression lines do not overlap (Figure 4).

The observed differences in CFs for all three peaks (5, 8, and 14) are statistically significant. Because of the relatively small contribution of Peaks 8 and 14 to the total PCB mass, it is expected that the differences for these peaks will not significantly affect comparability between Hudson River water column data collected historically with data collected as part of the RAMP. DB-1 peak 5, which showed also a statistically significant difference in CFs between 2003 and 2009, accounts for a large part (approximately 30%) of the total PCB mass observed in the

water column at these locations during the Phase 1 RAMP. In contrast, Peaks 8 and 14 account for a relatively small portion of the total PCB mass at these locations (approximately 1.5% and 1.6% respectively).

References

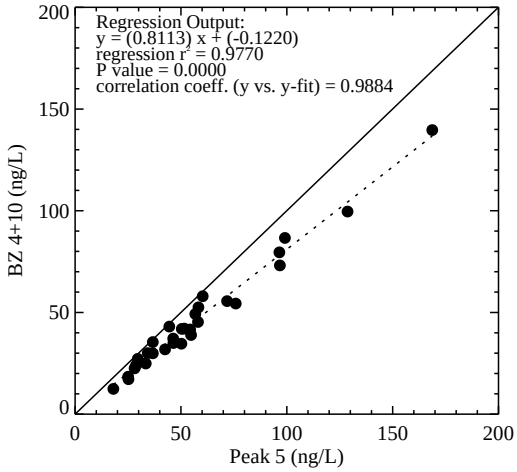
HydroQual 1997. *Development of Corrections for Analytical Biases in the 1991 – 1997 GE Hudson River PCB Database.* Prepared for General Electric Company Corporate Environmental Programs, Albany, NY. June 1997.

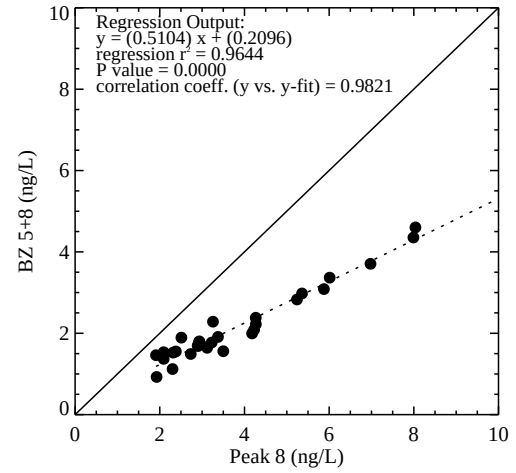
QEA/ESI 2004. *Technical Memorandum.* Prepared for General Electric Company Corporate Environmental Programs, Albany, NY. March 2004.

Table 1. 2009 Hudson River RAMP extracts selected for C18 analysis.

Field Sample ID	NEA ID	Location	Sample Type	Date Collected		Original NEA Reported (ng/L)				Coelution Bias Corrected (ng/L)[1]			
				Start	End	Total PCB	Peak 5	Peak 8	Peak 14	Total PCB	Peak 5	Peak 8	Peak 14
WFF-LOC5-090516-AT001	AM05399	Lock 5 Automated Station	24-hr Composite	05/15/09	05/16/09	60.8	25.2	1.91	0.865	50.0	15.4	0.688	1.09
WFF-LOC5-090517-BT001	AM05438	Lock 5 Automated Station	24-hr Composite	05/16/09	05/17/09	187	96.7	3.37	1.24	147	59.0	1.21	1.56
WFF-LOC5-090520-BT002	AM05572	Lock 5 Automated Station	24-hr Composite	05/19/09	05/20/09	144	56.8	5.24	1.80	119	34.6	1.89	2.27
WFF-LOC5-090528-DT004	AM06118RR2	Lock 5 Automated Station	24-hr Composite	05/27/09	05/28/09	339	169	10.6	2.19	267	103	3.81	2.76
WFF-LOC5-090529-CT001	AM06189	Lock 5 Automated Station	24-hr Composite	05/28/09	05/29/09	208	99.1	6.01	1.50	166	60.5	2.16	1.89
WFF-LOC5-090606-DT004	AM06871	Lock 5 Automated Station	24-hr Composite	06/05/09	06/06/09	81.2	34.3	2.93	0.818	66.2	20.9	1.06	1.03
WFF-LOC5-090607-DT001	AM06992	Lock 5 Automated Station	24-hr Composite	06/06/09	06/07/09	123	50.4	4.23	1.43	101	30.7	1.52	1.80
WFF-LOC5-090611-DT003	AM07580	Lock 5 Automated Station	24-hr Composite	06/10/09	06/11/09	115	58.0	3.23	1.00	90.3	35.4	1.16	1.26
WFF-LOC5-090612-DT002	AM07877	Lock 5 Automated Station	24-hr Composite	06/11/09	06/12/09	95.6	46.4	3.50	1.04	75.5	28.3	1.26	1.32
WFF-LOC5-090615-DT003	AM08032	Lock 5 Automated Station	24-hr Composite	06/14/09	06/15/09	152	50.2	4.18	1.61	130	30.6	1.51	2.02
WFF-BDUP-090521-BT001	AM05820	Stillwater Manual Station	Temporal Grab	05/21/09	NA	71.9	36.7	2.09	0.777	56.5	22.4	0.753	0.980
WFF-STWA-090521-BT001	AM05823	Stillwater Manual Station	Temporal Grab	05/21/09	NA	72.4	36.7	2.38	0.877	56.8	22.4	0.857	1.10
WFF-STWA-090604-BT001	AM06771	Stillwater Manual Station	Temporal Grab	06/04/09	NA	85.2	44.5	2.51	0.644	66.5	27.2	0.905	0.812
WFF-BDUP-090611-DT004	AM07850	Stillwater Manual Station	Temporal Grab	06/11/09	NA	107	58.3	2.89	0.785	82.2	35.5	1.04	0.989
WFF-STWA-090611-DT001	AM07852	Stillwater Manual Station	Temporal Grab	06/11/09	NA	110	60.3	2.91	0.800	85.0	36.8	1.05	1.01
WFF-TIDA-090612-DT004	AM07880	Thompson Island Dam Automated Station	24-hr Composite	06/11/09	06/12/09	106	46.3	4.27	1.38	85.7	28.3	1.54	1.74
WFF-TIDA-090614-DT001	AM08010	Thompson Island Dam Automated Station	24-hr Composite	06/13/09	06/14/09	151	54.8	6.98	2.09	126	33.4	2.51	2.63
WFF-TIDA-090615-DT001	AM08033	Thompson Island Dam Automated Station	24-hr Composite	06/14/09	06/15/09	137	54.3	5.36	1.87	113	33.1	1.93	2.36
WFF-TIDA-090616-DT001	AM08067	Thompson Island Dam Automated Station	24-hr Composite	06/15/09	06/16/09	155	51.6	8.04	2.48	130	31.5	2.89	3.13
WFF-TIDA-090619-AT001	AM08324	Thompson Island Dam Automated Station	24-hr Composite	06/18/09	06/19/09	217	96.5	7.99	2.44	175	58.9	2.88	3.08
WFF-WAFA-090528-DT001	AM06169	Waterford Automated Station	24-hr Composite	05/27/09	05/28/09	53.2	18.1	2.09	0.606	44.9	11.0	0.753	0.763
WFF-WAFA-090529-CT001	AM06244	Waterford Automated Station	24-hr Composite	05/28/09	05/29/09	148	71.8	3.26	0.971	118	43.8	1.17	1.22
WFF-WAFA-090529-BT001	AM06272RR1	Waterford Automated Station	24-hr Composite	05/28/09	05/29/09	239	129	5.88	1.04	186	78.5	2.12	1.32
WFF-WAFA-090531-DT001	AM06330	Waterford Automated Station	24-hr Composite	05/30/09	05/31/09	161	75.9	4.27	1.30	129	46.3	1.54	1.64
WFF-WAFA-090601-DT001	AM06371	Waterford Automated Station	24-hr Composite	05/31/09	06/01/09	94.9	42.5	2.93	1.01	76.7	25.9	1.06	1.28
WFF-WAFA-090602-DT001	AM06454	Waterford Automated Station	24-hr Composite	06/01/09	06/02/09	82.2	28.1	3.12	0.955	69.4	17.1	1.12	1.20
WFF-BDUP-090604-BT003	AM06768	Waterford Automated Station	24-hr Composite	06/03/09	06/04/09	58.6	25.0	1.93	0.569	47.7	15.3	0.693	0.717
WFF-WAFA-090605-AT003	AM06854	Waterford Automated Station	24-hr Composite	06/04/09	06/05/09	68.7	29.6	2.32	0.761	55.8	18.0	0.834	0.959
WFF-WAFA-090606-DT001	AM06987	Waterford Automated Station	24-hr Composite	06/05/09	06/06/09	77.8	33.4	2.73	0.870	63.3	20.4	0.983	1.10
WFF-WAFA-090608-DT001	AM07121	Waterford Automated Station	24-hr Composite	06/07/09	06/08/09	68.4	28.8	2.30	0.816	55.8	17.5	0.829	1.03

[1] *PCB peack concentrations after application of 2004 correction factors (QEA/ESI 2004)*





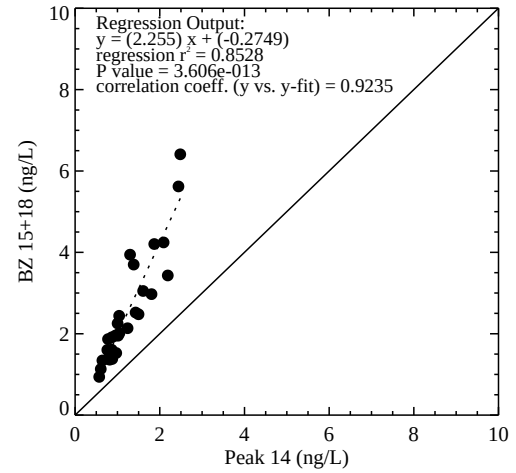


Figure 1. Regression of 2009 PCB peak concentrations in original (DB-1 column) and reanalyzed (C18 column) water column data.

Notes: Dotted line is the linear regression

SJRH - \\Nereus\E_Drive\090469-03_RAMP\Analysis\Bias_Correction\regression_2009_subset.pro
Thu Aug 06 15:30:02 2009

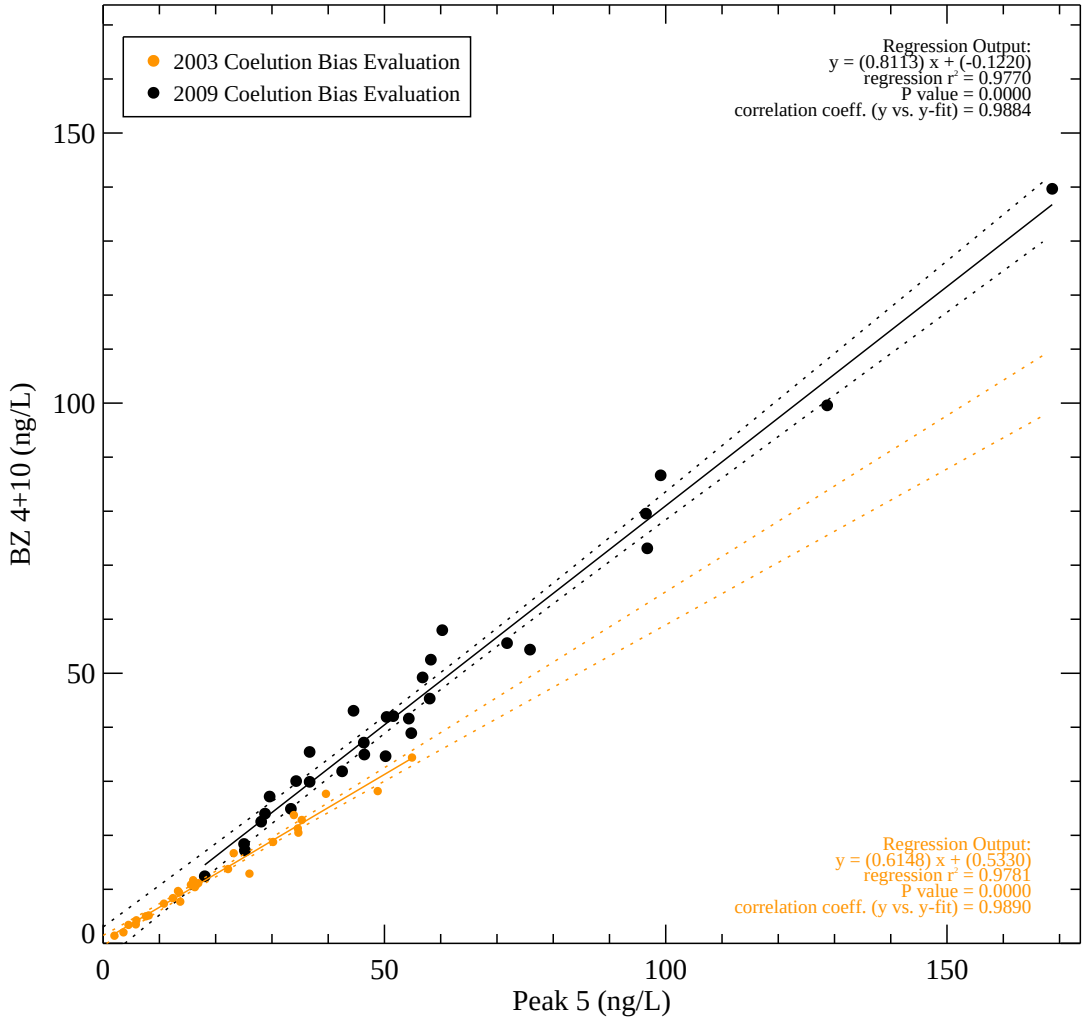


Figure 2. Comparison of 2003 and 2009 PCB peak 5 and BZ 4+10 concentrations in Hudson River water samples

Notes: 3 samples have been omitted. Dotted lines represent the 95% confidence interval on the regression line.

SJRH - \\Nereus\E_Drive\090469-03_RAMP\Analysis\Bias_Correction\Regression_2003_2009.pro
Thu Aug 06 15:24:51 2009

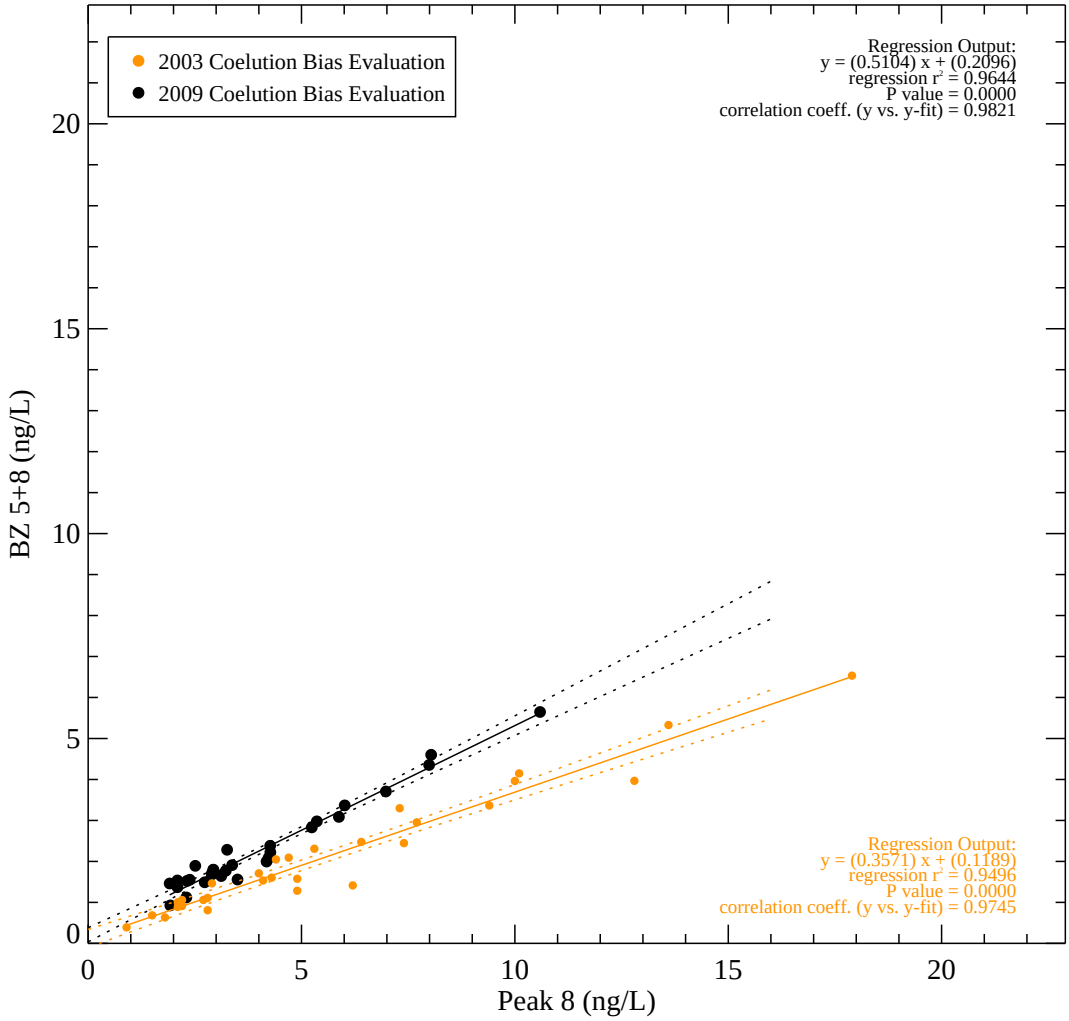


Figure 3. Comparison of 2003 and 2009 PCB peak 8 and BZ 5+8 concentrations in Hudson River water samples

Notes: Dotted lines represent the 95% confidence interval on the regression line.

SJRH - \\Nereus\E_Drive\090469-03_RAMP\Analysis\Bias_Correction\Regression_2003_2009.pro
Thu Aug 06 15:24:51 2009

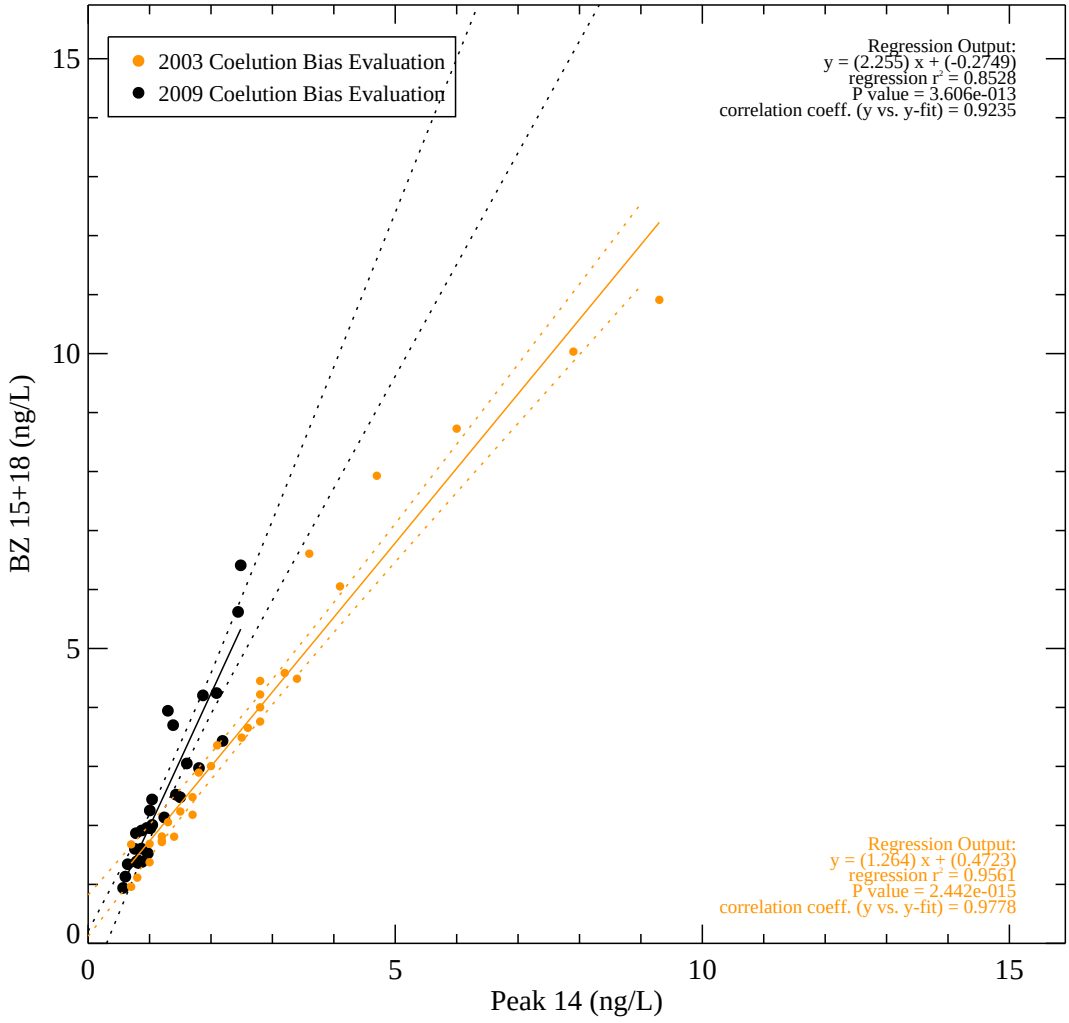


Figure 4. Comparison of 2003 and 2009 PCB peak 14 and BZ 15+18 concentrations in Hudson River water samples

Notes: Dotted lines represent the 95% confidence interval on the regression line.

SJRH - \\Nereus\E_Drive\090469-03_RAMP\Analysis\Bias_Correction\Regression_2003_2009.pro
Thu Aug 06 15:24:51 2009