Identification and Assessment of Polychlorinated Biphenyls (PCBs) in Storm Water in the Delaware Estuary

DELAWARE RIVER BASIN COMMISSION

Delaware River Basin Commission

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1 Executive Summary

From 2005 through 2007, the Delaware River Basin Commission (DRBC) collected 17 storm water samples from 5 different conveyances and analyzed the samples for all 209 PCB congeners, under a Persistent Bioaccumulative Toxics grant from the U.S. Environmental Protection Agency. DRBC collected both first-flush and flow-weighted composite samples from all sites, to compute event mean concentrations. We evaluated congener pattern similarities between paired samples and between samples and Aroclor mixtures. In comparison to storm water samples, equipment blank and decontamination water samples exhibited substantially lower PCB concentrations and dissimilar congener patterns. Computed event mean concentrations from this sampling generally agreed with literature derived values used in the Total Maximum Daily Loads in 2003 and 2006. We provided specific equipment recommendations to facilitate future storm water PCB monitoring.

2 Project Description

2.1 *Background*

Polychlorinated biphenyls (PCBs) are a class of man-made compounds that were manufactured and used extensively in electrical equipment such as transformers and capacitors, paints, printing inks, pesticides, hydraulic fluids, and lubricants. Although their manufacture and use was generally banned by federal regulations in the late 1970s, existing uses in electrical equipment and certain exceptions to the ban were allowed. In addition, PCBs may also be created as a by-product of certain manufacturing processes such as pigment and dye production. PCBs are hydrophobic, sorbing to organic particles such as soils and sediments and concentrating in the tissues of aquatic biota either directly or indirectly through the food chain.

PCBs are classified as a probable human carcinogen by the U.S. Environmental Protection Agency, and have been shown to effect reproduction, suppress the immune system, and are a possible endocrine disruptor. Starting in the late 1980s, the States of Delaware, New Jersey and Pennsylvania began issuing consumption advisories for portions of the Delaware Estuary for PCBs due to the level of PCBs observed in the tissues of resident and anadromous fish species. Advisories are currently in effect for the entire estuary from the head of tide at Trenton, NJ to the mouth of Delaware Bay. The advisories range from a one meal per year recommendation for all species taken between the C&D Canal and the DE-PA border to consumption of no more than one meal per month of striped bass or white perch in Zones 2 - 4.

In 2003, EPA Regions 2 and 3 issued a Total Maximum Daily Load (TMDL) for total PCBs in Zones 2 through 5 of the Delaware River. EPA issued a second TMDL for Zone 6 in December 2006.

DRBC applied for and received a $70,000 grant from the U.S. Environmental Protection Agency in 2002 drawing from Persistent Bioaccumulative Toxics (PBT) funding to identify and assess non-point sources of PCBs to the Delaware Estuary. To fulfill the grant requirements, DRBC collected storm water runoff samples from selected non-point source drainage areas, to calculated non-point source loadings.

The specific task associated with this project involves collection of storm water runoff samples from selected sub-basins and analysis of these samples for PCB congeners. Measured concentrations were used to compute event mean concentration (EMC) estimate. Computation of the EMCs will allow estimation of non-point source loads on a wider spatial and temporal scale.

2.2 *Sampling and Analysis*

Five storm water conveyances were sampled between June 2005 and October 2007, each during two different rainfall events equaling or exceeding 0.5" of rain over a 24 hour period. To allow for buildup of PCBs in the watershed, we targeted storm events preceded by 72 hours without measurable rainfall. Conveyances consisted of storm sewers, storm water channels, or intermittent streams with minimal baseflow. Sampling was performed by DRBC staff using an ISCO automated sampler (see Section 4 for deployment details). Through coordination with our state partners, we identified 5 locations for sampling, as shown in Table 1.

Table 1: Sample Locations

Sample Location	Rationale	Coordinates
Shellpot Creek downstream of North Market Street, Wilmington, DE	The watershed above the gage (01477800) is of mixed land use, with moderate slopes. Delaware issued a fish advisory for the lower Shellpot in 2002 due primarily to PCBs. A PCB TMDL for the Shellpot will need to be established by 2009. Close proximity to the gage will facilitate computation of loadings. A flow analysis performed by DNREC demonstrates that during storm events, the volume of stormwater runoff greatly exceeds the baseflow. Recommended by DNREC.	39°45'40.17"N 75°31'6.06"W
Mingo Creek Basin Philadelphia, PA	The drainage area covers airport and residential/commercial areas. Mingo impoundment is pumped down after storm events and discharged to the Schuylkill River. Recommended by PADEP.	39°53'41.14"N 75°13'44.00"W
State Rd. & Ashburner St. stormwater outfall to Pennypack Creek Philadelphia, PA	This is an MS4 (separate storm sewer) area of about 500 acres including about 80% residential and 20% industrial. Recommended by PADEP.	40° 2'11.16"N 75° 0'42.14"W
Stormwater outfall near Rancocas Creek Mt. Holly, NJ	This outfall represented a suburban mixed land use watershed. This site was also recommended by MHMUA to provide a comparison to measured WWTP effluent concentrations in Rancocas Creek.	39°59'50.44"N 74°48'14.72"W
DRBC Stormwater Retrofit Project	This site represents DRBC's effort to reduce both the volume and pollutant load of an existing stormwater system. In future phases of work we will be able to assess the load reduction associated with improved stormwater management. This site also provided ease of access, which is discussed in more detail in "Lessons Learned."	40°15'39.05"N 74°49'58.21"W

For each storm water conveyance sampled, two discrete volumes were collected during the first storm event, and one flow weighted composite sample was collected during the second storm event. During the first storm at a conveyance, a discrete sample volume representative of the first flush of storm water was collected at the onset of precipitation runoff, followed by a flow weighted composite sample for the remaining duration of runoff. During the second storm event at a conveyance, only flow weighted compositing was performed. Figure 1 shows a schematic representation of the sampling process design. Figure 2 depicts the hydrograph compositing approach for the different sample types.

Event mean concentrations (EMCs) were calculated for both storm events for each conveyance. Where separate first flush and flow weighted composites were collected, the EMC was calculated as follows:

$$EMC = \left(C_{ff} \times f_{ff}\right) + \left(C_{fwc} \times \left(1 - f_{ff}\right)\right)$$

where:

EMC	=	Event Mean Concentration
C_{ff}	=	Concentration measured in the “first flush” sample
f_{ff}	=	Estimated fraction of the volume discharged during first flush portion of the runoff event
C_{fwc}	=	Concentration measured in the flow weighted composite sample

Where a single flow weighted composite sample was collected, the EMC will be equal to the concentration measured in the sample.

Figure 1: Conceptual Monitoring Approach

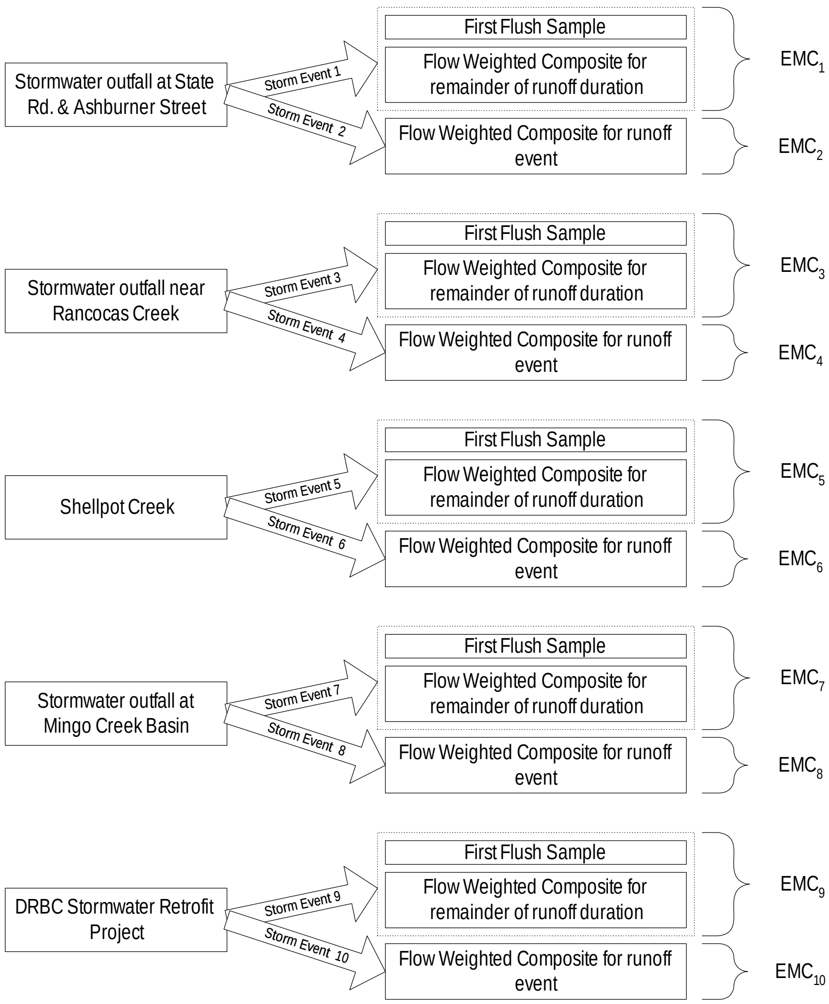
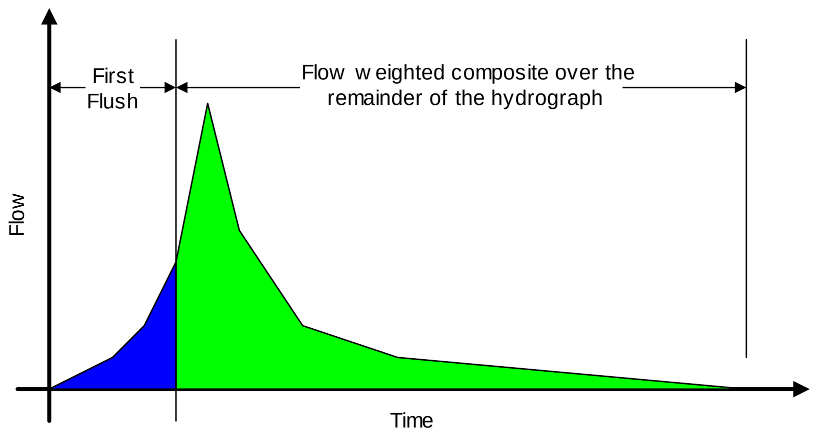
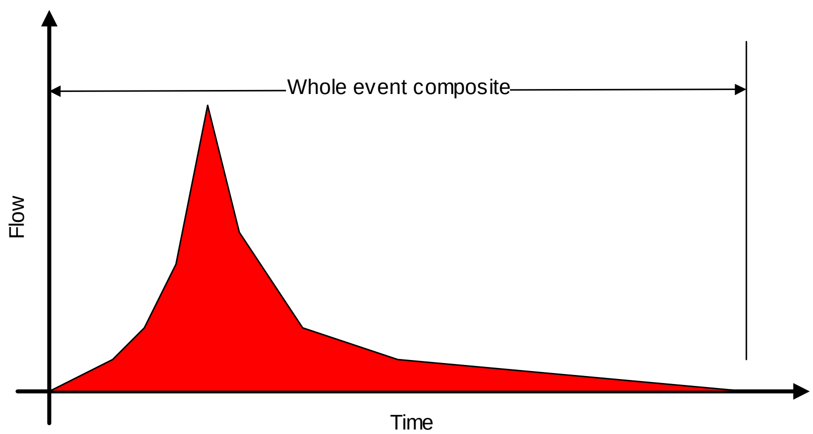


Figure 2: Schematic of Hydrograph Compositing

First Storm Event



Second Storm Event



3 Analytical Results

3.1 *Total PCBs by Location*

Table 2 below shows the total PCB results by sample location and date. The highest concentration was 145,310 pg/L measured at the outfall at State & Ashburner Streets. The lowest concentration of a stormwater sample (as opposed to a blank) was 3,941 pg/L measured at the DRBC stormwater retrofit basin. All locations demonstrated high variability between the site highest and lowest concentrations.

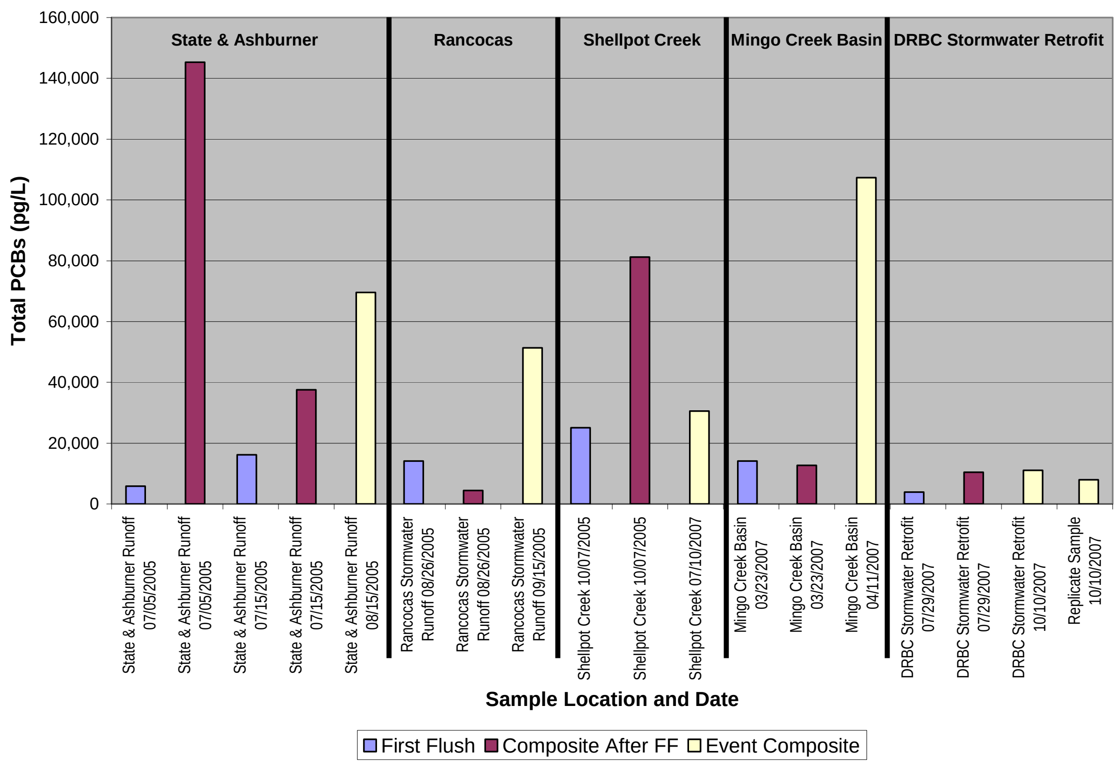
Table 2: Total PCBs by Location, Date, and Sample Type

Sample ID	Total PCBs (pg/L)	Date	Location	Type
SPD-FF-060905	512	6/9/2005	Equipment Blank	Blank
SPD-FF-070505	5,873	7/5/2005	State & Ashburner Runoff	First Flush
SAP-FWCR-070505	145,310	7/5/2005	State & Ashburner Runoff	Composite After FF
SPD-FF-071505	16,187	7/15/2005	State & Ashburner Runoff	First Flush
SAP-FWCR-071505	37,559	7/15/2005	State & Ashburner Runoff	Composite After FF
SAP-FWCR-081505	69,581	8/15/2005	State & Ashburner Runoff	Event Composite
MTH-FF-082605	410	8/26/2005	Equipment Blank	Blank
RAN-FF-082605	14,086	8/26/2005	Rancocas Stormwater Runoff	First Flush
RAN-FWCR-082605	4,447	8/26/2005	Rancocas Stormwater Runoff	Composite After FF
RAN-WHC-091505	51,322	9/15/2005	Rancocas Stormwater Runoff	Event Composite
MLP-092105	280	9/21/2005	Millipore Water Blank	Blank
WIL-FF-100605	841	10/6/2005	Equipment Blank	Blank
SPT-FF-100705	25,077	10/7/2005	Shellpot Creek	First Flush
SPT-FWCR-100705	81,248	10/7/2005	Shellpot Creek	Composite After FF
PBL-TWCR-021307	1,028	2/13/2007	Equipment Blank	Blank
MGC-FF-032307	14,136	3/23/2007	Mingo Creek Basin	First Flush
MGC-TWCR-032307	12,686	3/23/2007	Mingo Creek Basin	Composite After FF
PEN-TWCR-041107	1,137	4/11/2007	Equipment Blank	Blank
MGC-TWCR-041107	107,332	4/11/2007	Mingo Creek Basin	Event Composite
FLA-FWCR-062207	771	6/22/2007	Equipment Blank	Blank
SHP-FWCD-071007	30,584	7/10/2007	Shellpot Creek	Event Composite
DRB-FF-072907	3,941	7/29/2007	DRBC Stormwater Retrofit	First Flush
DRB-FWCR-072907	10,455	7/29/2007	DRBC Stormwater Retrofit	Composite After FF
DRB-FWC-101007	11,029	10/10/2007	DRBC Stormwater Retrofit	Event Composite
FRB-FWC-101007	8,013	10/10/2007	Replicate Sample	Replicate

First flush samples did not exhibit notably higher concentrations than composite samples of either the remainder of the event or composite samples of a whole event, as shown in Figure 3. In fact, the only instances of a higher first flush concentration were observed at the Rancocas site on August 26, 2005 and Mingo Creek Basin on March 23, 2007. In all other instances, the first flush concentration was lower than the composite of the remainder of the storm.

Equipment blanks were generally low (410 to 1,137 pg/L) with the highest values observed in blanks collected in 2007 for Mingo Creek.

Figure 3: Total PCB Chart by Sample Type



3.2 *Inter-Sample Comparison of Congener Patterns*

Analysis of all 209 congeners allows a simple and effective method of comparing congener patterns of individual samples. We normalized the congener concentration in each sample by the total PCB concentration for that sample (i.e., converted to proportional concentration). We then compared the normalized congener proportion of each sample to the congener proportion of every other sample using a simple similarity coefficient, the correlation coefficient. After eliminating any congeners which were non-detect in all samples, we calculated the correlation between each pair of samples and squared this value to get the R^2 (coefficient of determination) between each pair (note: we did not expect any negative correlations in these samples, so the squared value provided a more readily interpretable coefficient). Table 3 below shows the computed R^2 value (i.e., our measure of similarity) for each pair. Pairs with R^2 greater than or equal to 0.9 are highlighted. Note, of course, that along the spine of the matrix, each sample is in perfect correlation (similarity) with itself, as is customary with similarity matrices. For this comparison, we removed blank sample results. However, blank sample comparisons will be discussed at length later in the report

A review of Table 3 shows that most samples correlated well with other samples from the same site, as would be expected. Some sites showed similar congener patters as other sites. Mingo Creek Basin, for example demonstrated a similar congener pattern to both the Rancocas site and the State & Ashburner site. By contrast, the DRBC Stormwater Retrofit congener pattern was similar to the Shellpot and Mingo Creek Basin sites, but less similar to other sites.

Table 3: Correlation Matrix of Sample Results

			DRB-FF-072907	DRB-FWC-101007	DRB-FWCR-072907	FRB-FWC-101007	MGC-FF-032307	MGC-TWCR-032307	MGC-TWCR-041107	RAN-FF-082605	RAN-FWCR-082605	RAN-WHC-091505	SAP-FWCR-070505	SAP-FWCR-071505	SAP-FWCR-081505	SHP-FWCD-071007	SPD-FF-070505	SPD-FF-071505	SPT-FF-100705	SPT-FWCR-100705
DRBC Stormwater Retrofit	First Flush	DRB-FF-072907	1.00	0.90	0.93	0.89	0.93	0.89	0.87	0.71	0.84	0.79	0.83	0.87	0.83	0.88	0.76	0.82	0.67	0.55
DRBC Stormwater Retrofit	Event Composite	DRB-FWC-101007		1.00	0.99	0.99	0.93	0.82	0.94	0.66	0.84	0.78	0.82	0.86	0.85	0.97	0.70	0.72	0.64	0.47
DRBC Stormwater Retrofit	Composite After FF	DRB-FWCR-072907			1.00	0.99	0.95	0.85	0.94	0.69	0.87	0.80	0.85	0.88	0.88	0.97	0.74	0.76	0.68	0.52
Replicate Sample	Replicate	FRB-FWC-101007				1.00	0.93	0.83	0.93	0.67	0.86	0.79	0.84	0.87	0.87	0.97	0.73	0.73	0.68	0.51
Mingo Creek Basin	First Flush	MGC-FF-032307					1.00	0.97	0.89	0.86	0.95	0.92	0.95	0.97	0.93	0.88	0.86	0.90	0.77	0.65
Mingo Creek Basin	Composite After FF	MGC-TWCR-032307						1.00	0.79	0.93	0.94	0.95	0.96	0.98	0.90	0.76	0.90	0.95	0.79	0.72
Mingo Creek Basin	Event Composite	MGC-TWCR-041107							1.00	0.63	0.78	0.75	0.76	0.81	0.81	0.94	0.64	0.67	0.56	0.39
Rancocas Stormwater Runoff	First Flush	RAN-FF-082605								1.00	0.88	0.96	0.90	0.91	0.82	0.57	0.86	0.92	0.75	0.70
Rancocas Stormwater Runoff	Composite After FF	RAN-FWCR-082605									1.00	0.91	0.98	0.96	0.95	0.79	0.95	0.91	0.89	0.78
Rancocas Stormwater Runoff	Event Composite	RAN-WHC-091505										1.00	0.93	0.95	0.87	0.70	0.84	0.90	0.72	0.63
State & Ashburner Runoff	Composite After FF	SAP-FWCR-070505											1.00	0.98	0.95	0.75	0.95	0.93	0.88	0.79
State & Ashburner Runoff	Composite After FF	SAP-FWCR-071505												1.00	0.93	0.78	0.90	0.94	0.82	0.73
State & Ashburner Runoff	Event Composite	SAP-FWCR-081505													1.00	0.81	0.88	0.86	0.81	0.69
Shellpot Creek	Event Composite	SHP-FWCD-071007														1.00	0.65	0.63	0.58	0.42
State & Ashburner Runoff	First Flush	SPD-FF-070505															1.00	0.91	0.93	0.89
State & Ashburner Runoff	First Flush	SPD-FF-071505																1.00	0.84	0.78
Shellpot Creek	First Flush	SPT-FF-100705																	1.00	0.94
Shellpot Creek	Composite After FF	SPT-FWCR-100705																		1.00

Cell highlighted when $R^2 > 0.9$

Figures 4 through 6 below show the relative proportion of each congener for two samples collected at Mingo Creek Basin and a sample collected at Shellpot Creek. The similarities in congener patterns are evident not only between the two Mingo Creek Basin samples, but also between Mingo Creek and Shellpot, suggesting that common Aroclor mixtures contribute to the PCB loads in both systems.

Figure 4: Mingo Creek First Flush Congener Pattern, March 23, 2007

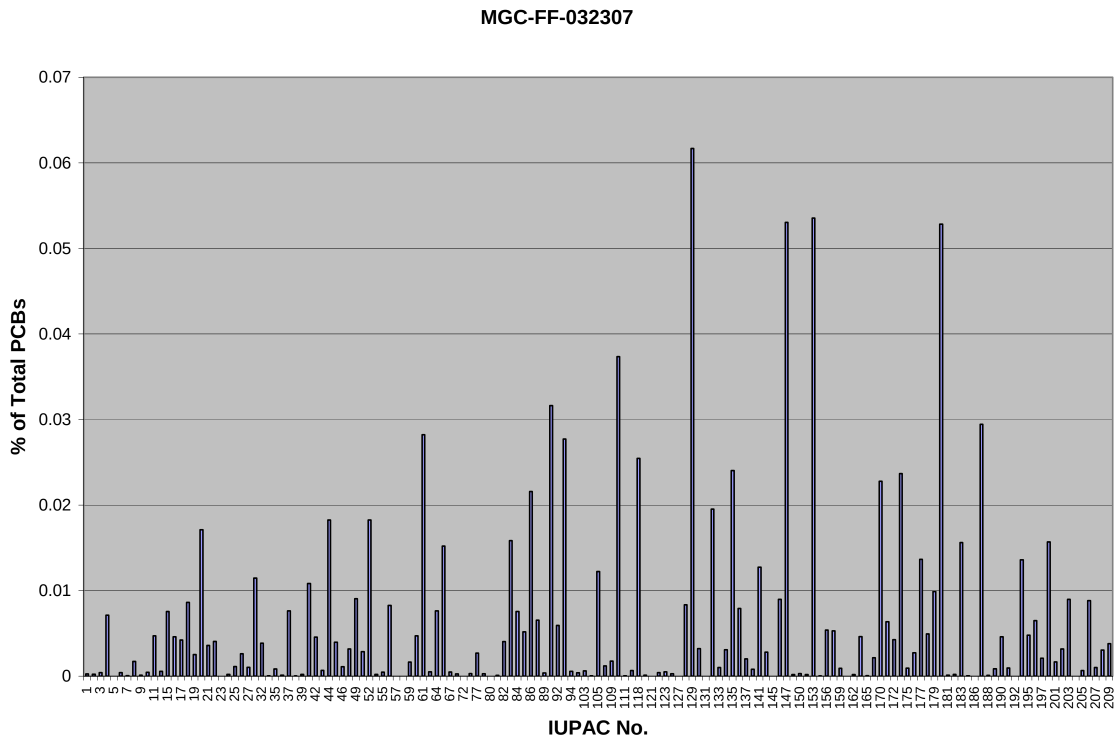


Figure 5: Mingo Creek Composite of the Remainder Congener Pattern March 23, 2007

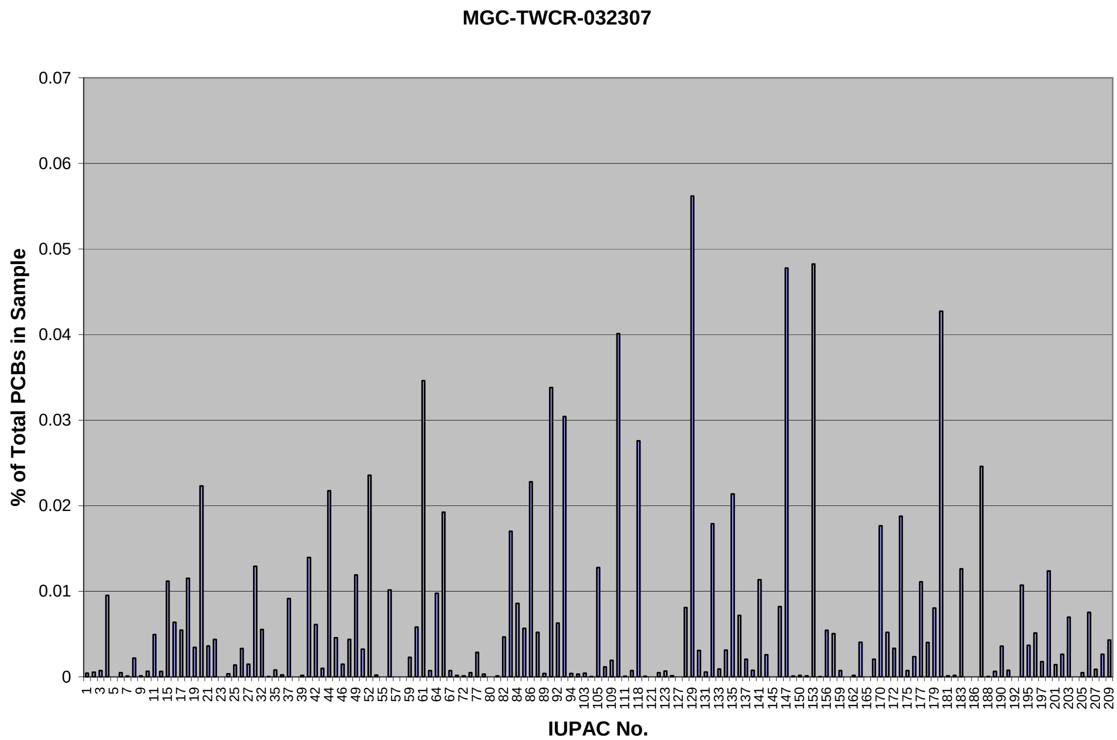
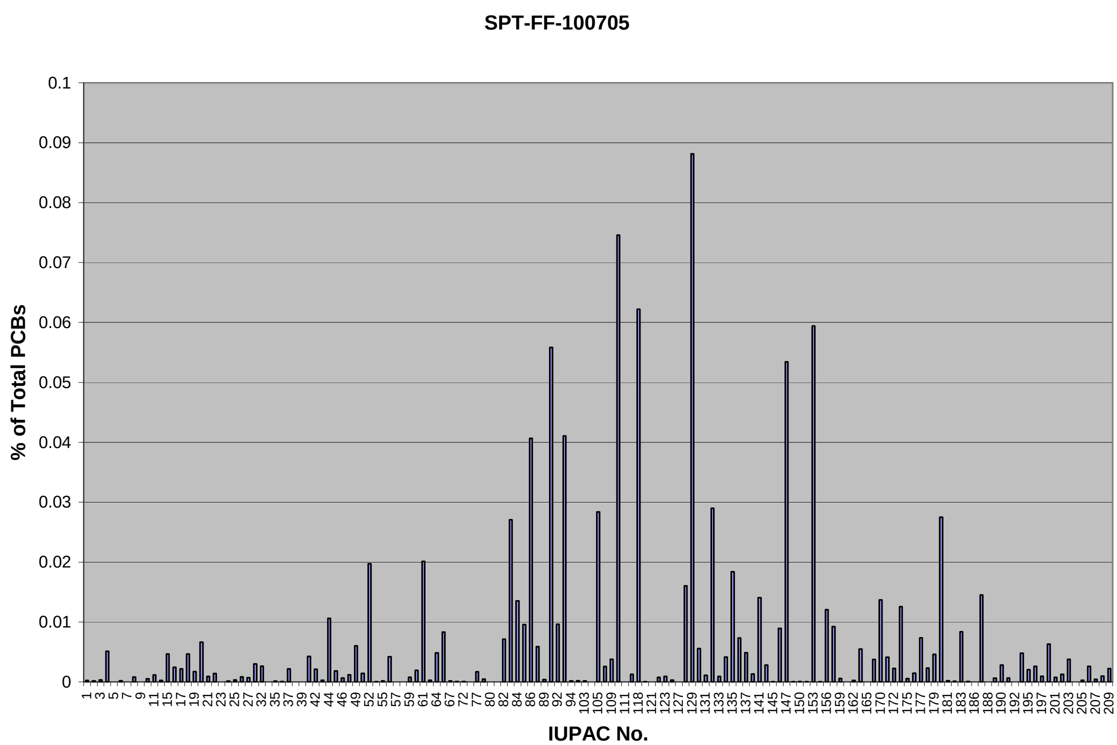


Figure 6: Shellpot Creek First Flush Congener Pattern October 7, 2005



3.3 *Comparison of Sample Congener Patterns to Aroclors*

Using the same approach described in the previous section, we compared normalized congener patterns from our stormwater samples to normalized congener patterns from Aroclors, as measured by Rushneck (2004). Again, we performed similarity analysis for each pairing of stormwater and Aroclor, computing the coefficient of determination (R^2) for each pair. Table 4 below shows the computed R^2 value for each pair. Pairs with R^2 greater than or equal to 0.5 are highlighted. This threshold is lower than the sample to sample comparison, as we expect distortions of the Aroclor patterns in the stormwater due to mixtures and weathering.

Table 4: Correlation Matrix for Samples and Aroclors

Sample Source	Sample ID	AROCLOR 1221	AROCLOR 1232	AROCLOR 1016	AROCLOR 1242	AROCLOR 1248	AROCLOR 1254	AROCLOR 1260	AROCLOR 1262	AROCLOR 1268
DRBC Stormwater Retrofit	DRB-FF-072907	0.002	0.002	0.015	0.035	0.081	0.426	0.787	0.558	0.000
DRBC Stormwater Retrofit	DRB-FWC-101007	0.000	0.000	0.000	0.001	0.019	0.328	0.917	0.698	0.004
DRBC Stormwater Retrofit	DRB-FWCR-072907	0.002	0.002	0.001	0.001	0.026	0.371	0.904	0.670	0.002
Equipment Blank	FLA-FWCR-062207	0.584	0.876	0.145	0.143	0.028	0.022	0.009	0.002	0.004
Replicate Sample	FRB-FWC-101007	0.002	0.004	0.002	0.000	0.016	0.359	0.912	0.666	0.002
Mingo Creek Basin	MGC-FF-032307	0.003	0.000	0.005	0.028	0.117	0.506	0.760	0.516	0.004
Mingo Creek Basin	MGC-TWCR-032307	0.003	0.004	0.022	0.074	0.220	0.595	0.616	0.379	0.001
Mingo Creek Basin	MGC-TWCR-041107	0.002	0.001	0.000	0.002	0.023	0.256	0.889	0.710	0.005
Millipore Water Blank	MLP-092105	0.796	0.801	0.061	0.062	0.015	0.010	0.000	0.000	0.002
Equipment Blank	MTH-FF-082605	0.430	0.494	0.067	0.065	0.014	0.080	0.328	0.266	0.000
Equipment Blank	PBL-TWCR-021307	0.200	0.816	0.387	0.384	0.094	0.036	0.026	0.014	0.004
Equipment Blank	PEN-TWCR-041107	0.121	0.334	0.106	0.138	0.089	0.319	0.324	0.148	0.005
Rancocas Stormwater Runoff	RAN-FF-082605	0.003	0.007	0.024	0.106	0.345	0.619	0.424	0.234	0.000
Rancocas Stormwater Runoff	RAN-FWCR-082605	0.003	0.001	0.000	0.011	0.113	0.660	0.650	0.376	0.001
Rancocas Stormwater Runoff	RAN-WHC-091505	0.003	0.002	0.013	0.071	0.274	0.523	0.571	0.356	0.000
State & Ashburner Runoff	SAP-FWCR-070505	0.003	0.000	0.002	0.026	0.161	0.673	0.607	0.363	0.007
State & Ashburner Runoff	SAP-FWCR-071505	0.003	0.001	0.011	0.048	0.184	0.597	0.646	0.404	0.001
State & Ashburner Runoff	SAP-FWCR-081505	0.003	0.001	0.000	0.007	0.087	0.560	0.682	0.442	0.019
Shellpot Creek	SHP-FWCD-071007	0.002	0.008	0.008	0.003	0.003	0.287	0.960	0.768	0.006
Equipment Blank	SPD-FF-060905	0.234	0.832	0.337	0.321	0.052	0.026	0.024	0.012	0.005
State & Ashburner Runoff	SPD-FF-070505	0.002	0.000	0.002	0.021	0.155	0.798	0.499	0.243	0.000
State & Ashburner Runoff	SPD-FF-071505	0.003	0.010	0.042	0.107	0.260	0.685	0.477	0.265	0.000
Shellpot Creek	SPT-FF-100705	0.002	0.002	0.002	0.003	0.077	0.834	0.450	0.167	0.001
Shellpot Creek	SPT-FWCR-100705	0.002	0.000	0.000	0.011	0.152	0.962	0.289	0.074	0.004
Equipment Blank	WIL-FF-100605	0.055	0.074	0.012	0.017	0.017	0.231	0.484	0.303	0.000

Highlighting indicates $R^2 > 0.5$

In general, surface water samples showed a higher correlation to Aroclors 1254, 1260, and 1262, while equipment blanks patterns were more closely related to Aroclors 1221 and 1232. DRBC stormwater retrofit samples showed a signal of Aroclors 1260 and 1262. State & Ashburner samples appeared to be a mixture of Aroclor 1254 and 1262, while Mingo Creek Basin exhibited similarities to all 3 common industrial Aroclors (1254, 1260, and 1262).

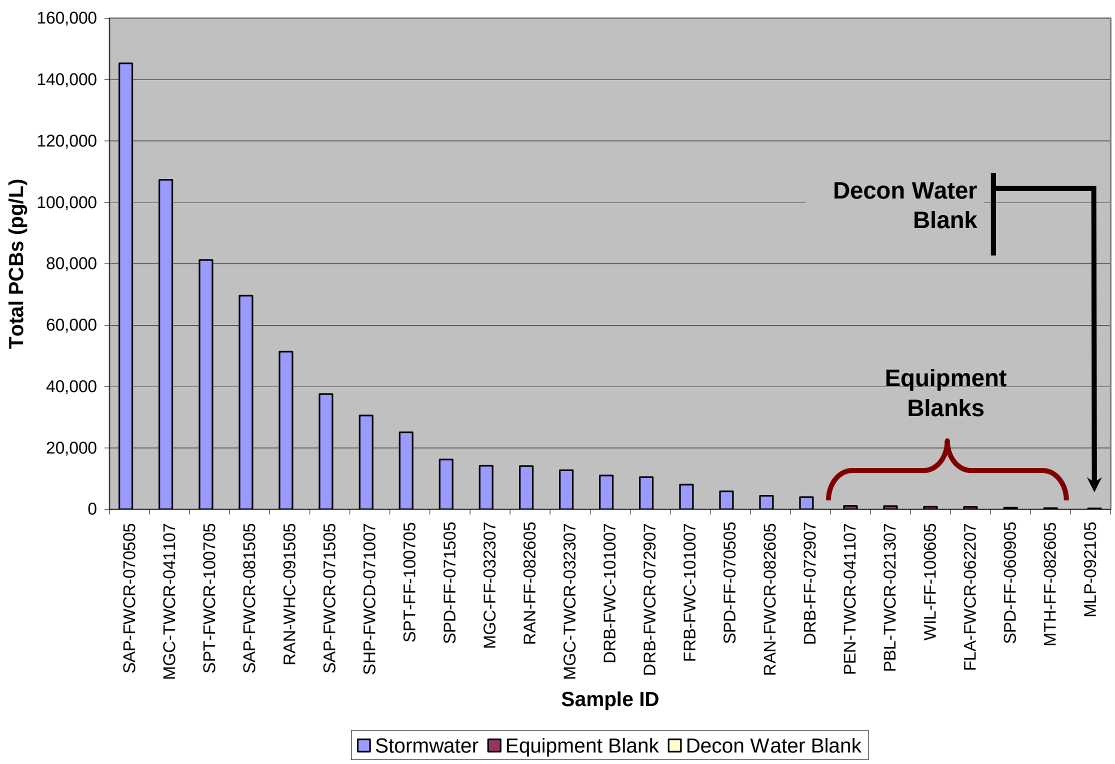
Interestingly, when Shellpot Creek was sampled in 2005, results exhibited primarily a signal from 1254. When resampled in 2007 however, the congener pattern appeared to be dominated by 1260 with some 1262 as well. These results could indicate the introduction of a new PCB source in the period between sampling events.

3.4 *Assessment of Blanks*

Six equipment blank samples, generated by pumping Millipore ultrapure water through the ISCO sampler after decon, were analyzed for PCB congeners. Equipment blank samples were typically generated for each sample location, prior to deployment. In addition to the equipment blank samples, we submitted a sample of the Millipore ultrapure water directly from the dispenser, without contacting the ISCO sampler, to determine the baseline concentration.

A review of the blank data shows that equipment blanks were all substantially lower than stormwater samples. Equipment blank total PCB concentrations ranged from 410 pg/L to 1,137 pg/L. The lowest stormwater concentration was more than three times the concentration of the highest equipment blank sample, although those two samples were not collected as part of the same deployment. The Millipore ultrapure water blank had a total PCB concentration of 280 pg/L. Figure 7 below shows the ranking of all stormwater and blank concentrations for total PCBs.

Figure 7: Total PCB Concentrations in Stormwater and Blank Samples



Even more important than the total PCB concentration in the blanks is the congener distribution. We performed the similarity analysis of normalized congener concentrations described earlier for all blanks as well as stormwater samples. In Table 5 below, blank samples are highlighted in blue. Note that blank results correlated poorly with stormwater samples, as a consequence of dissimilar congener patterns. In fact, the median r^2 value for blank to stormwater pairs was 0.04. Blanks did correlate well with other blanks, suggesting that the source of congeners in the blanks was different than the source of congeners in stormwater samples.

Table 5: Correlation Matrix of Blank Results

	DRB-FF-072907	DRB-FWC-101007	DRB-FWCR-072907	FLA-FWCR-062207	FRB-FWC-101007	MGC-FF-032307	MGC-TWCR-032307	MGC-TWCR-041107	MLP-092105	MTH-FF-082605	PBL-TWCR-021307	PEN-TWCR-041107	RAN-FF-082605	RAN-FWCR-082605	RAN-WHC-091505	SAP-FWCR-070505	SAP-FWCR-071505	SAP-FWCR-081505	SHP-FWCD-071007	SPD-FF-060905	SPD-FF-070505	SPD-FF-071505	SPT-FF-100705	SPT-FWCR-100705	WIL-FF-100605
DRB-FF-072907	1.00	0.90	0.93	0.05	0.89	0.93	0.89	0.87	0.01	0.39	0.12	0.50	0.71	0.84	0.79	0.83	0.87	0.83	0.88	0.11	0.76	0.82	0.67	0.55	0.55
DRB-FWC-101007		1.00	0.99	0.03	0.99	0.93	0.82	0.94	0.01	0.37	0.07	0.40	0.66	0.84	0.78	0.82	0.86	0.85	0.97	0.06	0.70	0.72	0.64	0.47	0.46
DRB-FWCR-072907			1.00	0.02	0.99	0.95	0.85	0.94	0.00	0.34	0.06	0.40	0.69	0.87	0.80	0.85	0.88	0.88	0.97	0.05	0.74	0.76	0.68	0.52	0.48
FLA-FWCR-062207				1.00	0.01	0.03	0.04	0.02	0.94	0.72	0.81	0.52	0.03	0.02	0.02	0.02	0.03	0.02	0.01	0.83	0.03	0.04	0.02	0.02	0.22
FRB-FWC-101007					1.00	0.93	0.83	0.93	0.00	0.32	0.04	0.37	0.67	0.86	0.79	0.84	0.87	0.87	0.97	0.04	0.73	0.73	0.68	0.51	0.44
MGC-FF-032307						1.00	0.97	0.89	0.00	0.31	0.08	0.46	0.86	0.95	0.92	0.95	0.97	0.93	0.88	0.06	0.86	0.90	0.77	0.65	0.48
MGC-TWCR-032307							1.00	0.79	0.01	0.29	0.10	0.49	0.93	0.94	0.95	0.96	0.98	0.90	0.76	0.08	0.90	0.95	0.79	0.72	0.45
MGC-TWCR-041107								1.00	0.00	0.34	0.05	0.38	0.63	0.78	0.75	0.76	0.81	0.81	0.94	0.05	0.64	0.67	0.56	0.39	0.50
MLP-092105									1.00	0.64	0.60	0.37	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.63	0.01	0.01	0.01	0.01	0.15
MTH-FF-082605										1.00	0.62	0.71	0.20	0.25	0.24	0.24	0.27	0.25	0.34	0.63	0.22	0.25	0.17	0.12	0.55
PBL-TWCR-021307											1.00	0.58	0.09	0.06	0.07	0.06	0.07	0.04	0.04	0.96	0.07	0.12	0.04	0.04	0.22
PEN-TWCR-041107												1.00	0.40	0.42	0.39	0.41	0.44	0.38	0.37	0.56	0.45	0.45	0.38	0.38	0.78
RAN-FF-082605													1.00	0.88	0.96	0.90	0.91	0.82	0.57	0.07	0.86	0.92	0.75	0.70	0.31
RAN-FWCR-082605														1.00	0.91	0.98	0.96	0.95	0.79	0.05	0.95	0.91	0.89	0.78	0.41
RAN-WHC-091505															1.00	0.93	0.95	0.87	0.70	0.05	0.84	0.90	0.72	0.63	0.35
SAP-FWCR-070505																1.00	0.98	0.95	0.75	0.05	0.95	0.93	0.88	0.79	0.39
SAP-FWCR-071505																	1.00	0.93	0.78	0.06	0.90	0.94	0.82	0.73	0.42
SAP-FWCR-081505																		1.00	0.81	0.04	0.88	0.86	0.81	0.69	0.42
SHP-FWCD-071007																			1.00	0.03	0.65	0.63	0.58	0.42	0.51
SPD-FF-060905																				1.00	0.05	0.10	0.04	0.03	0.22
SPD-FF-070505																					1.00	0.91	0.93	0.89	0.40
SPD-FF-071505																						1.00	0.84	0.78	0.36
SPT-FF-100705																							1.00	0.94	0.34
SPT-FWCR-100705																								1.00	0.30
WIL-FF-100605																									1.00

Cell highlighted when $R^2 > 0.7$

The figures below show the congener distributions for an equipment blank (Figure 8) and the corresponding stormwater sample from the same deployment (Figure 9). Note the prevalence of lower chlorinated congeners in the equipment blank result which are largely absent from the stormwater sample. Overall for the entire project, equipment blank congener patterns tended to be shifted toward lower chlorinated congeners, consistent with Aroclors 1221 and 1232, as opposed to the stormwater samples which appeared to be more consistent with Aroclors 1254, 1260, and 1262.

Figure 8: Equipment Blank Congener Pattern from August 2005

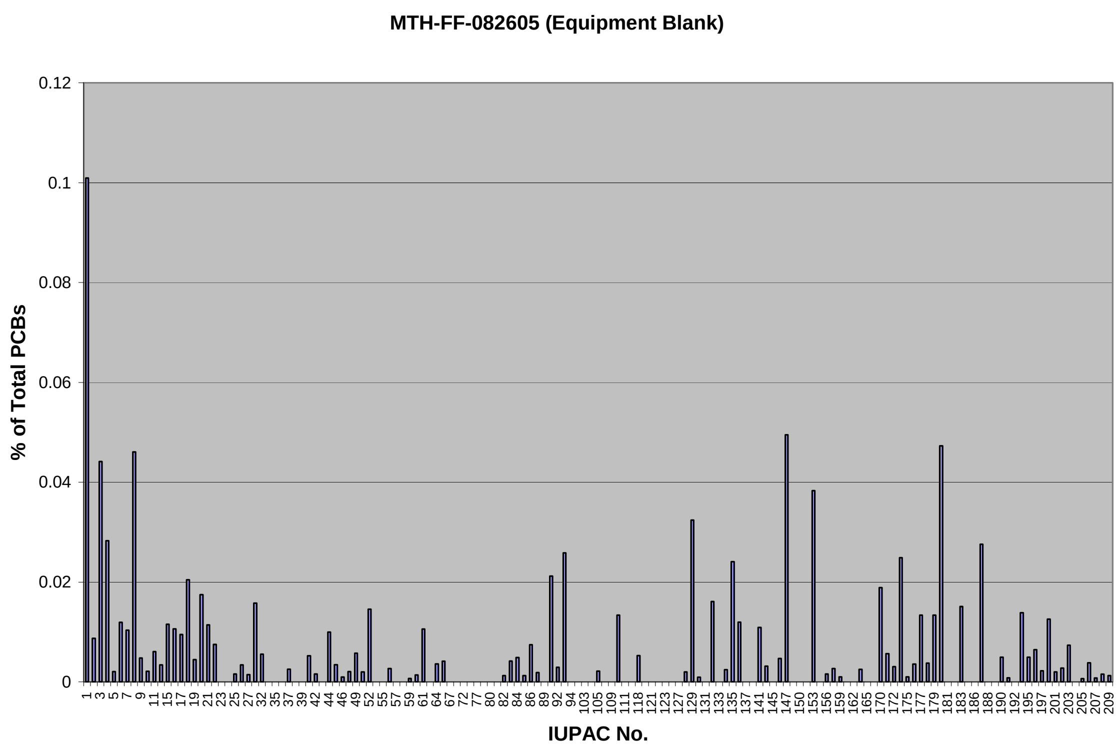
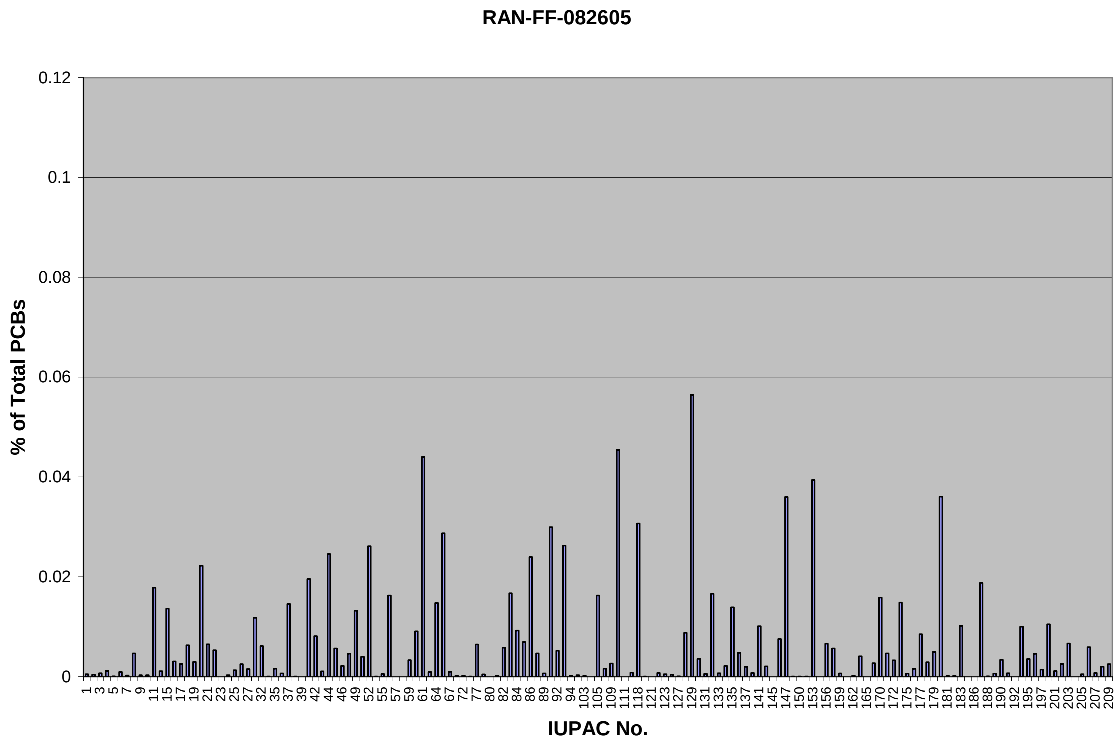


Figure 9: Stormwater Sample Congener Pattern from August 2005



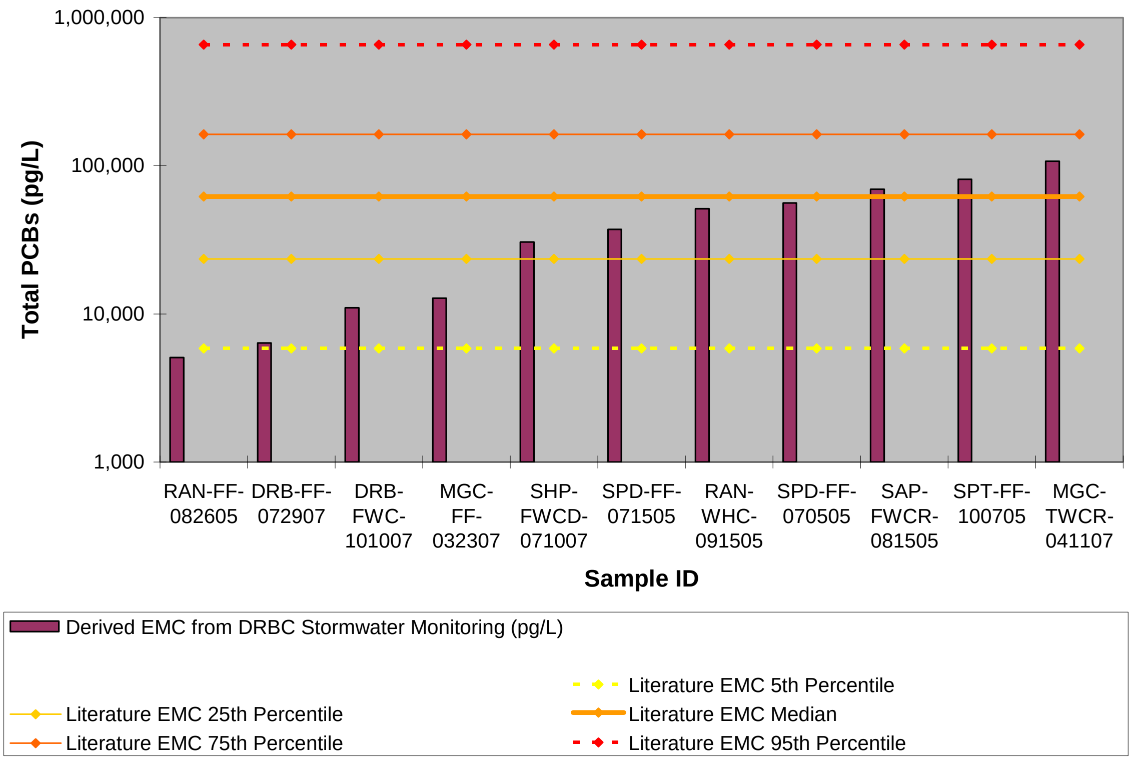
4 Comparison to Stage 1 PCB TMDL Stormwater EMCs

The EMC is defined as the total mass load of a chemical parameter yielded from a site during a storm divided by the total runoff water volume discharged during the event. For the Stage 1 PCB TMDL, EMCs for PCBs were developed through a collaborative literature search performed by Philadelphia Water Department, CDM, and DuPont, with the EMC database being developed and maintained by DuPont.

The literature review team collected and reviewed more than 100 articles and reports dating from 1979 to the present. Articles and reports covered data from over 130 station storms from 70 sites in 20 cities in Canada, the U.S., France, Germany, and Japan. Of the 100+ articles reviewed, 12 yielded useful runoff data.

We computed EMCs from the stormwater data collected under this project, as described in a previous section. We compared these new EMCs to the literature derived EMCs from the Stage 1 PCB TMDL. Figure 10 below shows the new sample specific EMCs and quantiles of the literature EMCs. The new EMCs agree well with the literature derived values. The new EMCs are mostly within the range between the 5th and 75th percentile. The median EMC value from the stormwater measurements is 37,285 pg/L total PCBs, compared to the literature derived median of 61,990 pg/L. The lower values of the current EMCs seem intuitively reasonable considering the length of time that has passed since PCB manufacturing was banned and the age of the literature values.

Figure 10: Comparison of Computed EMCs from DRBC Stormwater Monitoring to Literature Derived EMCs from Stage 1 PCB TMDL



5 Lessons Learned

An important goal of this project was to test the concept of low level PCB congener sampling using an automated monitor, and report back on lessons learned from the effort. The sections below include general recommendations applicable to similar efforts.

5.1 *Sample Equipment*

Through trial and error, the sample collection team discovered several modifications to the standard ISCO setup which greatly improved the likelihood of successful sample collection

5.1.1 Suction Hose

The standard Teflon lined suction hose sold by ISCO was problematic for these deployments. ISCO's Teflon lined suction line was a composite made from a hard outer shell lined with a thin interior Teflon tube. In our deployments, the Teflon tube easily separated from the outer shell. In addition, we found that the outer shell easily developed small cracks that resulted in a loss of suction during deployment. We found that any kinking of the tubing resulted in a crack in the hose. Given the challenges of deployment, we found it nearly impossible to prevent all kinks in the suction line.

Alternatively, we found solid FEP tubing sold by Fischer Scientific that provided much more dependable performance. We used 3/8-inch inner diameter, 7/16-inch outer diameter tubing in 25-foot lengths (Fischer catalog number 14 176 272). We found that this tube could be inserted into the pump tubing, instead of using the steel connector. This eliminated an additional item of equipment contacting the sample, which we found to be desirable. We secured the connection with a hose clamp applied to the exterior of the pump tubing.

5.1.2 Battery

The ISCO 12-volt Ni-Cad battery did not provide sufficient prolonged power for our deployments. During test deployments we found that the battery power drained before the full sampling program was completed. Because we used a bubble line depth sensor, our deployments consumed more power than a deployment using a sonic or pressure transducer sensor. The power drain was compounded when storms arrived later than predicted.

For actual deployments, we used a deep cycle marine battery. ISCO sells a cable adapter to connect to such a power source. About mid way through the project, we replaced the existing fuse holder on the adapter cable with a fuse holder from an electronic supply chain store, to allow use of standard size off-the-shelf fuses (with the same rating as the ISCO fuses). This allowed us to obtain replacement fuses in a more timely manner.

5.1.3 Bottles

For our project, we selected a four bottle array. ISCO sells clear glass bottles sized specifically to fit the four bottle array. The ISCO bottles, however, presented two concerns. First, the bottles are clear, not amber glass, as called for in method 1668A. Amber glass is typically called for when photo interference could influence analytical results. While it is unclear that this is the case with PCBs, our preference was to remain consistent with the method. Secondly, the ISCO bottles were clearly priced to be reused, rather than shipped to the lab and later discarded. If we reused the bottles, it would have been necessary to decon the bottles between deployments and to transfer the sample from the ISCO bottles to the final sample bottle. Both of these steps would have added risk of cross contamination.

We found that wide mouth 2.5 liter amber glass jars from Environmental Sampling Supply (ESS catalog number 2500-0050) could be used in the 4 bottle array with some added care. Specifically, the opening of the ESS bottles is smaller than that of the ISCO bottles. We found that is was necessary to level the ISCO sampler, to ensure that all sample water entered the bottle. The ESS jars can be purchased pre-cleaned and certified and samples could be shipped to the lab without transfer to a secondary container.

5.1.4 Bubble Line Depth Sensor

Although the bubble line depth sensor performed very well, we modified our approach to avoid deployments when there was any threat of a frost. Our bubble line apparently accumulated moisture, possibly from the deployment at Shellpot Creek when higher than forecasted rainfall resulted in minor flooding that washed the ISCO from its deployment location. During a later deployment, overnight temperatures fell below freezing, causing the moisture inside the bubble line meter to freeze and rupture an internal pressure tube, resulting in a costly and time consuming repair.

5.2 *Site Selection*

Site selection presented numerous challenges. Identifying accessible sites with suitable flow conditions proved difficult and time consuming.

In June 2006, we deployed the ISCO sampler at Shellpot Creek in Wilmington, Delaware. Two major rain events in close succession caused major flooding on the Delaware River and many tributaries. The first of these rain events was much larger than forecasted, and caused isolated tributary flooding, including high water in Shellpot Creek. The ISCO sampler, which was deployed during the first storm event, was inundated and washed from it’s mooring at the discontinued USGS gaging platform. As a result, the pumping motor was damaged. We attempted to repair the motor, in consultation with Teledyne ISCO technical representatives, but ultimately had to replace the motor. Unfortunately, this maintenance work left the unit unusable for much of that summer.

In summer 2007, we deployed the ISCO in a manhole in Camden, near the Delaware River. We discovered that the manhole was tidally influenced, and that during high tide, water in the manhole inundated the invert of the incoming pipe to a depth of more than one foot. This made it impossible to obtain a sample from the pipe that was free of cross contamination from the Delaware River. This site was therefore abandoned.

In future sampling applications, we will allocate more time to site selection and coordination with local contacts. This part of the overall effort proved more time consuming than we anticipated. In addition, we would allow greater funding for structural enhancements and armoring to facilitate deployments. Although we successfully completed the planned sampling, constructed platforms and support apparatus would have decreased the frequency of failed sampling attempts.

5.3 *Deployment*

As we progressed through the monitoring program, we found that programming the ISCO sampler in the controlled environment of the lab was preferable to programming in the field. Once on site, we reviewed the program, making minor adjustments if necessary.

6 Recommendations for Future Work

DRBC has continued to work closely with EPA Regions 2 and 3, New Jersey, Pennsylvania, and Delaware on initiatives to reduce PCB loadings to the Delaware Estuary to achieve the zone-specific TMDLs. These initiatives include close coordination of Pollutant Minimization Plans for point dischargers and development of implementation strategies for point and non-point sources. In order to track the effectiveness of these initiatives, periodic monitoring over multi-year intervals should be performed at the same sites identified in this project. In addition, identification of other sampling locations and subsequent monitoring could help to identify previously undiscovered sources of PCBs requiring control.

7 References

Delaware River Basin Commission. (2006). Revised Calibration of the Water Quality Model for the Delaware Estuary for Penta-PCBs and Carbon. http://www.state.nj.us/drbc/TMDL/RevisedModelCalibrationReport090506.pdf

Rushneck, D.R., Beliveau, A., Fowler, B., Hamilton, C., Hoover, D., Kaye, K., Berg, M., Smith, T., Telliard, W.A., Roman, H., Ruder, E., Ryan, L. (2004). Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA Method 1668A. *Chemosphere* **54** (2004) 79-87.