Appendix A1 – Summary of the City’s CSO Sampling Program to Date

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A1. Summary of the City's CSO Sampling Program to Date

In an effort to better understand the impacts of CSOs on the Canal and to the enhance the analytically limited data obtained by EPA (as noted in the City's comments to CSTAG and NRRB as well as in the City's current technical comments), the City has implemented a sampling program where the four largest CSOs, representing 90% of the CSO discharge to the Canal, and the two main waste water treatment plants (WWTP), receiving waste water and storm water from the watersheds draining to the Canal, were sampled for chemical and physical characteristics. A more limited sampling program was conducted at the three smaller CSOs believed to be impacted by NAPL from National Grid's Fulton MGP site or NAPL contaminated groundwater discharging to the CSOs. Water sampling at each CSO and WWTP was conducted for dual phases, dissolved and suspended matter fractions for organic compounds, and whole water and dissolved phase fraction for inorganic constituents. These samples were obtained consistent with the program's Quality Assurance Project Plan (QAPP) and its revisions (Louis Berger & Associates, PC, 2012, ibid 2013). This document provides a summary of the results of the physical characteristics and COPC concentrations in the CSOs and WWTPs obtained by the City to date. The City is continuing the efforts described in the QAPP to further expand our understanding of these discharges.

A1-1. Sampling Events

Wet weather samples collected in the field at the CSOs and WWTPs were obtained as time-composited whole water samples. For wet weather events, CSO samples were composited during the approximate duration of the storm once the initial CSO discharge was observed. For WWTPs, wet weather samples were initiated approximately one hour after CSO discharges had begun and collected as a time composite over the next 2 to 4-hour period, depending upon the estimated length of the rainfall event. Dry weather sampling at the WWTPs and three potentially impacted CSOs was conducted after a sustained period of dry weather of at least three days. Samples were again time composited over a four hour period to characterize the COPC concentrations in the domestic wastewater and dry-weather flow carried by the small CSOs.

Wet Weather Sampling

Six wet weather sampling events were conducted at the four major CSO and the two WWTPs, Red Hook and Owls Head. Table A1-1 summarizes the wet weather sampling events.

Table A1-1: Summary of Wet Weather Sampling Events

Event	Sampling Date	RH-035	OH-007	RH-034	RH-031	RH-WWTP	OH-WWTP
WW-1	09/28/12	✓	✓	✓	✓		
WW-2	01/11/13	✓	✓				
WW-3	01/16/13	✓	✓			✓	✓
WW-4	01/31/13	✓	✓	✓	✓	✓	✓
WW-5	02/11/13			✓			
WW-6	02/26/13			✓			

Dry Weather Sampling

Two dry weather sampling events were conducted at the potentially impacted CSOs near the Fulton MGP Site (RH-033, RH-037 and RH-038), a background CSO not influenced by the MGP site (RH-038) and the Red Hook and Owls Head WWTPs. Table A1-2 summarizes the dry weather sampling events.

Table A1-2: Summary of Dry Weather Sampling Events

Event	Sampling Date	RH-033	RH-036	RH-037	RH-038	NPS	RH-WWTP	OH-WWTP
DW-1	12/12/12	✓	✓	✓		✓		
DW-2	01/08/13	✓	✓	✓	✓	✓	✓	✓

Analytical data for the wet weather CSO and WWTP sampling events and for the dry weather WWTP sampling event are presented in Section A.1.2. Note that the City is still awaiting results for the samples obtained from the impacted CSO, which will be presented in subsequent data reports.

A1-2. Analytical Data Summary

A1-2.1. Total Suspended Solids

As part of CSO sampling, 4-liter whole water time composite samples were collected to assess the total suspended solids (TSS) concentration during an overflow event. Figure A1-1 shows the TSS concentration by sampling location and Figure A1-2 shows the TSS concentrations by wet weather events. The figures also present the average TSS concentration of each data group (*i.e.*, location or event).

During wet weather conditions the average TSS concentration for CSO and WWTPs is 200 mg/L (standard error of the mean (SE) 40 mg/L) and 167 mg/L (SE 63 mg/L), respectively. TSS concentration in domestic wastewater (*i.e.*, WWTP dry weather samples) is on average 145 mg/L (SE 5 mg/L). A review of Figure A1-1 shows a wide variation in TSS concentrations at each station. Organizing the data by event in Figure A1-2 shows that much of the variation can be explained by sampling event. Figure A1-2 shows substantive differences in TSS among sampling events but much less variation of TSS across stations within the same event. These results suggest that TSS is controlled system wide, probably by the ratio of storm water to municipal waste at the time of discharge.

A1-2.2. Physical Characteristics

Grain size evaluation of CSO and WWTP solids are predominantly fine grained solids ranging from clays to fine silts (1.4 to 63 microns). Figure A1-3 presents the fine grained solids content less than 63 um by sampling location. The fine grained solids content observed for CSOs and for WWTPs are on average 64 percent (SE 2.5 percent) and 68 percent fines (SE 3 percent), respectively, during wet weather conditions. Data for the single dry weather WWTP sampling event shows that the fine grained solids content of domestic wastewater is 63 percent at the Owls Head WWTP and 35 percent at the Red Hook WWTP.

A1-2.3. Total Organic Carbon

The total organic carbon (TOC) content in the CSO discharge was calculated using the particulate organic carbon (POC) and dissolved organic carbon (DOC) values. The POC accounts for 99.9 percent of the TOC. The TOC on the CSO solids was calculated as the quotient of POC and the corresponding TSS values. Figure A1-4 shows the TOC percentage on the CSO solids by sampling location.

The average TOC concentration during wet weather conditions for CSO and WWTP solids is approximately 40 percent (SE 2 percent) and 37 percent (SE 4 percent), respectively. The average TOC during dry weather conditions for WWTP solids is approximately 46 percent (SE 0.5 percent), which is comparable to that observed during wet weather conditions. This observation and the observation that TS concentrations are comparable under wet and dry conditions across CSOs and the WWTP influents suggest that solids in CSOs are predominantly from domestic wastewater.

A1-2.4. PAHs

PAH concentration, primary and alkylated PAHs, in the CSO discharge was measured for dissolved and particulate phases. Figures A1-5 to A1-22 show the concentration for the total PAH (TPAH)[1] and 17 individual PAHs (2-methylnaphthalene and the 16 priority PAHs) measured in the CSO discharge, the percent fraction in suspended phase and the concentration on solids. The PAH concentration on the solids was calculated using the PAH concentration in suspended phase and the corresponding TSS measured for that event. The TPAH concentration in the CSO discharge, shown in Figure A1-5a, is on an average 7 ug/L (SE 1.5 ug/L), with 70% of the TPAH mass on the particulate phase on an average. Similar levels are observed in WWTP during wet weather conditions, average 6 ug/L (SE 3 ug/L). Average TPAH concentration in CSO and WWTP solids in wet weather conditions is approximately 30 mg/kg (SE 3 mg/kg) and 27 mg/kg (SE 4 mg/kg), respectively. During dry weather, the TPAH concentration in WWTP solids is approximately 6 mg/kg (SE 1.5 mg/kg), a factor of five lower than the TPAH concentrations in wet weather. This pattern of decreased concentrations of PAHs on dry weather WWTP influent solids was observed for most individual PAH compounds as well.

Figure A1-23 presents the fraction of low molecular weight (LMW) PAHs in TPAH. Evaluation of the pattern of the PAHs indicate that in wet weather conditions the LMW PAHs are approximately 25 percent (SE 2 percent) of the TPAH concentration as opposed to 55 percent (SE 4 percent) during dry weather conditions. At 6 percent organic carbon, the TPAH concentration in the solids from CSOs is approximately 5 mg/kg (SE 2.3 mg/kg), four times lower than the preliminary remediation goal (PRG) for the site (Figure A1-24).

A1-2.5. PCBs

PCB concentrations in the CSO discharge and domestic wastewater were characterized for the dissolved and suspended solids phases using PCB congener analysis. The average wet weather CSO solids Total PCB (TPCB)[2] concentration is 0.42 mg/kg (SE 0.06 mg/kg).

Figures A1-25a and b show the concentration of TPCB measured in the CSO discharge and WWTP influent (dry and wet weather) on a whole water basis, the fraction on suspended solids and the concentration on the suspended solids. Notably, all CSO and WWTP concentrations on suspended solids

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[1] Total PAH is calculated as sum of the 17 PAHs, which include the 16 priority PAHs and 2,-methylnaphthalene. The sum was calculated using only the detected values. Non-detect values are not included in the total.

[2] Total PCB concentration is calculated as the sum of 209 congeners. Non-detect values are not included in the total.

are on average below the PRG for PCBs on sediments specified by EPA. The average CSO solids TPCB concentration at OH-007 is approximately two times higher than concentrations at RH-031, RH-034, and RH-035. The average TPCB concentration in the solids for WWTP is 0.34 mg/kg (SE 0.09 mg/kg) is comparable to that observed in solids from CSOs. The TPCB concentration in the domestic wastewater (average 0.07 mg/kg, 0.03 mg/kg), however, is a factor of six lower than the TPCB concentration observed in wet weather conditions.

A1-2.6. Metals

Whole water samples were collected during the wet weather and dry weather events to characterize the metals concentrations in CSO discharge in the influent to the WWTPs under wet and dry weather. This data was analyzed for whole water and dissolved concentrations of metals. Metals concentrations in the solid phase were calculated as the difference of the total and dissolved concentrations times the corresponding TSS measurements. For the solids concentration calculation which is based on the difference between whole water and dissolved phase samples, non-detected values were taken as zero. However, detection limits were sufficiently low that most metals of concern were detected in both analyses. Figures A1-26 to A1-34 show the concentration of iron, aluminum, and seven other metals, identified by EPA in the Remedial Investigation (RI) as metals of potential concern, for CSO and WWTP concentration on the solids. For each metal, two diagrams are presented in each figure. The first presents the whole water concentration as mass per unit volume. The second presents the calculated metals concentrations on suspended solids in the samples (C_{ss}) calculated as:

$$C_{ss} = \frac{(C_{whole\ water} - C_{dissolved})}{TSS}$$

Figure A1-26 shows the iron concentration in CSO discharge and WWTP. The average iron concentration on CSO solids is 18,000 mg/kg (SE 6,500 mg/kg) which is comparable to the concentration on solids from the WWTPs during wet weather conditions (average 18,000 mg/kg, SE 4,000 mg/kg). The iron concentration on suspended solids in dry weather, domestic waste water, is 9,000 mg/kg and 2,000 mg/kg for the Red Hook and Owls Head WWTPs, respectively.

A comparison of the whole water and suspended solids metal concentrations shows a substantial reduction in the amount of variance for metals concentration on suspended solids relative to whole water. For example, nearly all iron is particle-borne in all samples and thus varies with the amount of TSS. Dividing each result by the TSS concentration (see equation above) essentially eliminates the variability attributable to TSS variation. This reduction in variance occurred for nearly all metals examined, including aluminum, copper, lead, mercury and nickel, indicating that each of these metals is strongly associated with the suspended solids. For barium, dividing by the TSS increased the variance overall, although a few stations still seemed less variable after the calculation. Note that barium concentrations in the dissolved phase were essentially equal to the whole water concentrations for half of the samples and approximately 70 percent of the whole water concentrations for the other half of the samples; suggesting that barium is not strongly associated to suspended solids. Cadmium and silver fell in between the two groups of metal behavior with no apparent overall change in variability as indicated by the range of values for each station on whole water of suspended solids basis.

The data presentations in Figures A1-26 to A1-34 also permit a comparison among CSO, dry weather WWTP and wet weather WWTP solids-borne concentrations. For all metals the CSO solids and the wet weather solids-borne concentrations were all comparable, as was expected since they all represent the integration of stormwater and municipal solids. In comparison to dry weather solids, the wet weather and

CSO solids for iron, aluminum, copper and lead were notably higher than the concentrations of these metals on dry weather solids. The other metals were comparable in concentration among all three solids types although values were also variable, making detection of real differences difficult. Based on these data presentations, the CSO station at OH-007 tended to be higher in concentration per unit solids for some metals but not all.

A1-3. Additional Planned Sampling

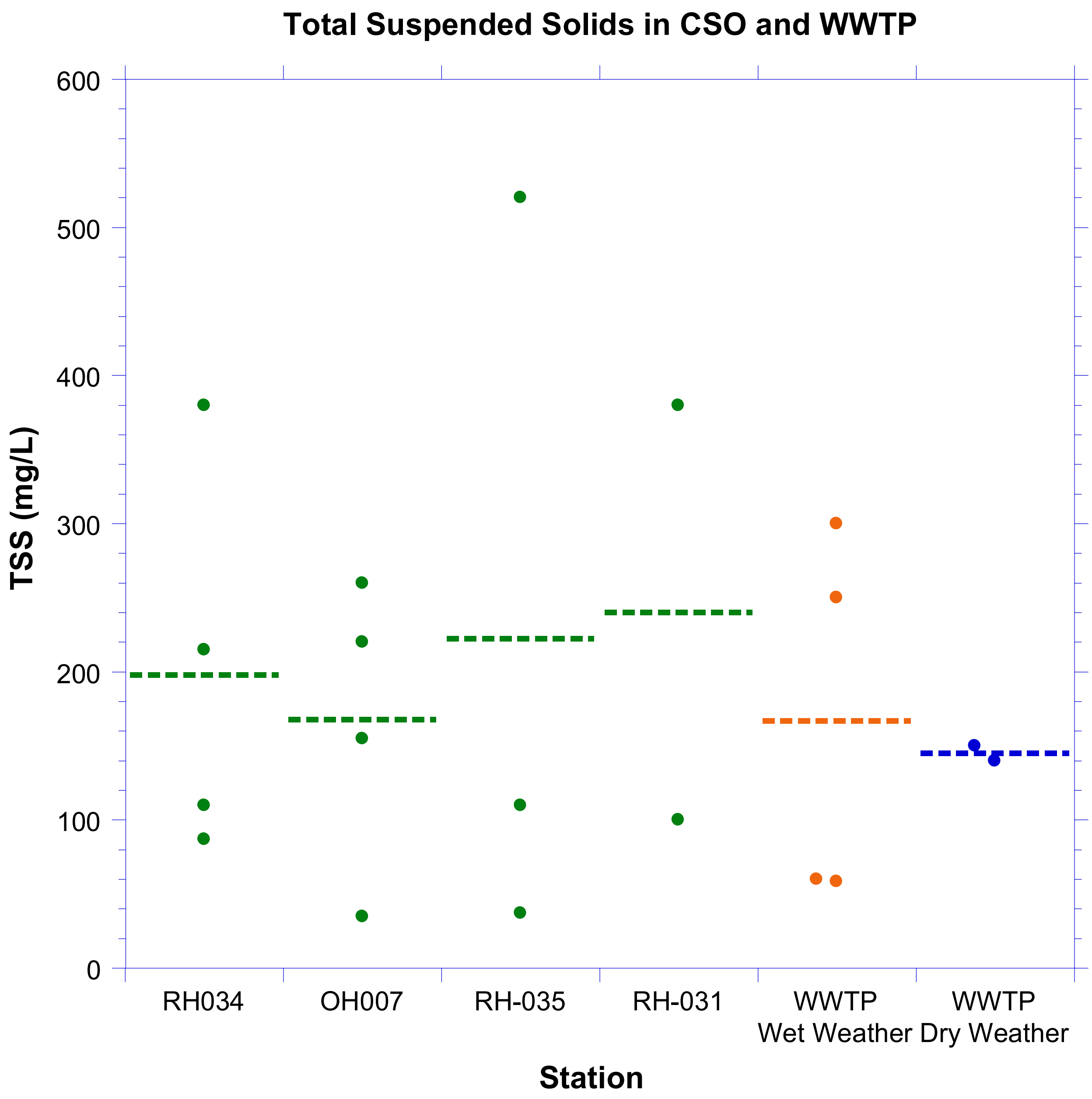
The sampling program proposed in the QAPP 2013 is still being implemented by the City. Additional planned sampling events include:

- CSO Sampling at the four large outfalls
- WWTP sampling for dry weather events
- Sampling to assess impact of the MGP/NAPL on CSOs

The City will submit a data summary report after the programs are implemented and validated data is received by the City.

References:

Louis Berger & Associates, PC, 2013. Quality Assurance Project Plan for Environmental Investigations at the Gowanus Canal Superfund Site.



Total Suspended Solids Concentrations in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-1

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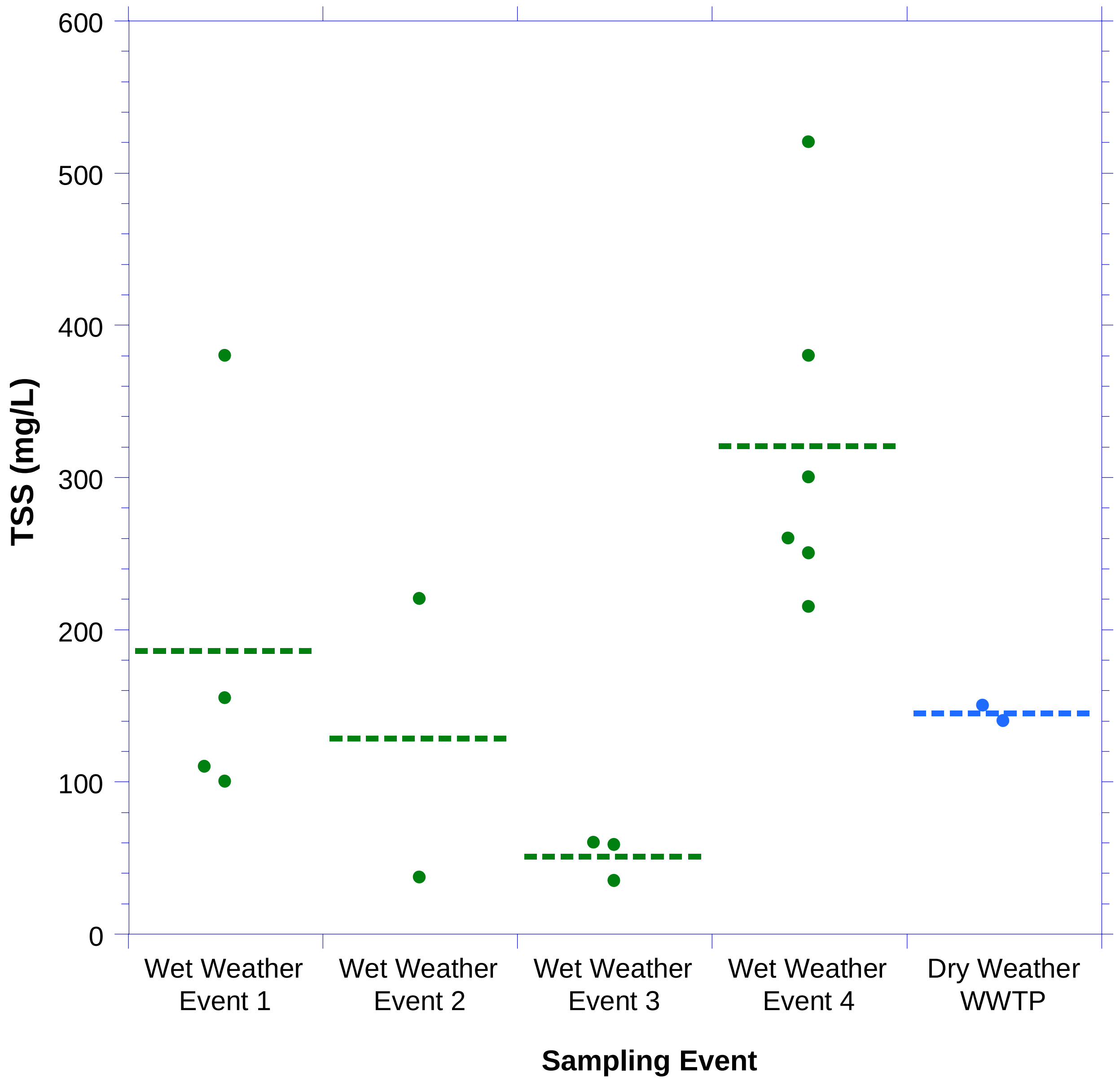

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Total Suspended Solids Concentrations by Sampling Event

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Figure A1-2

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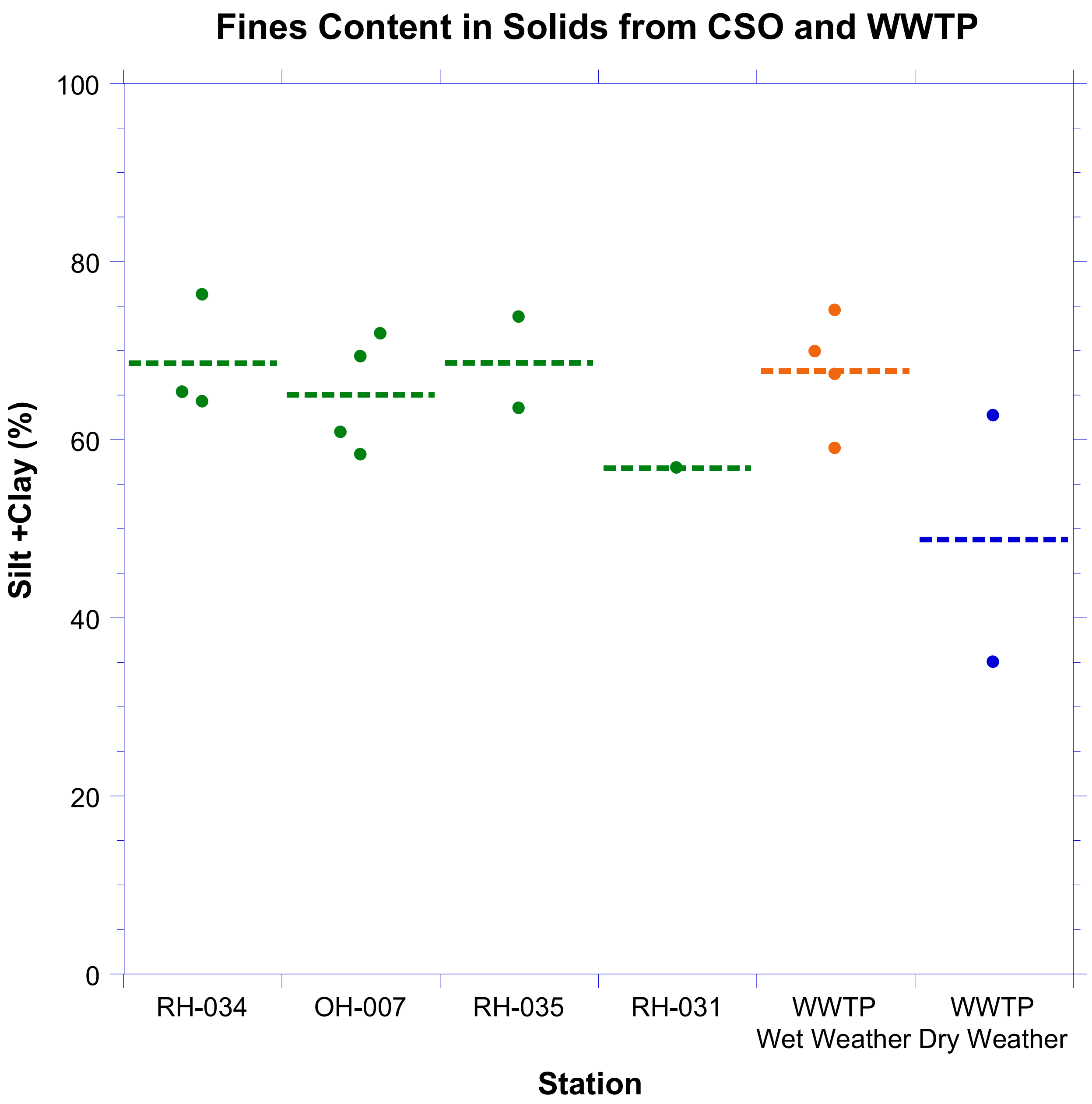

Fines Content in Solids from CSO and WWTP

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Figure A1-3

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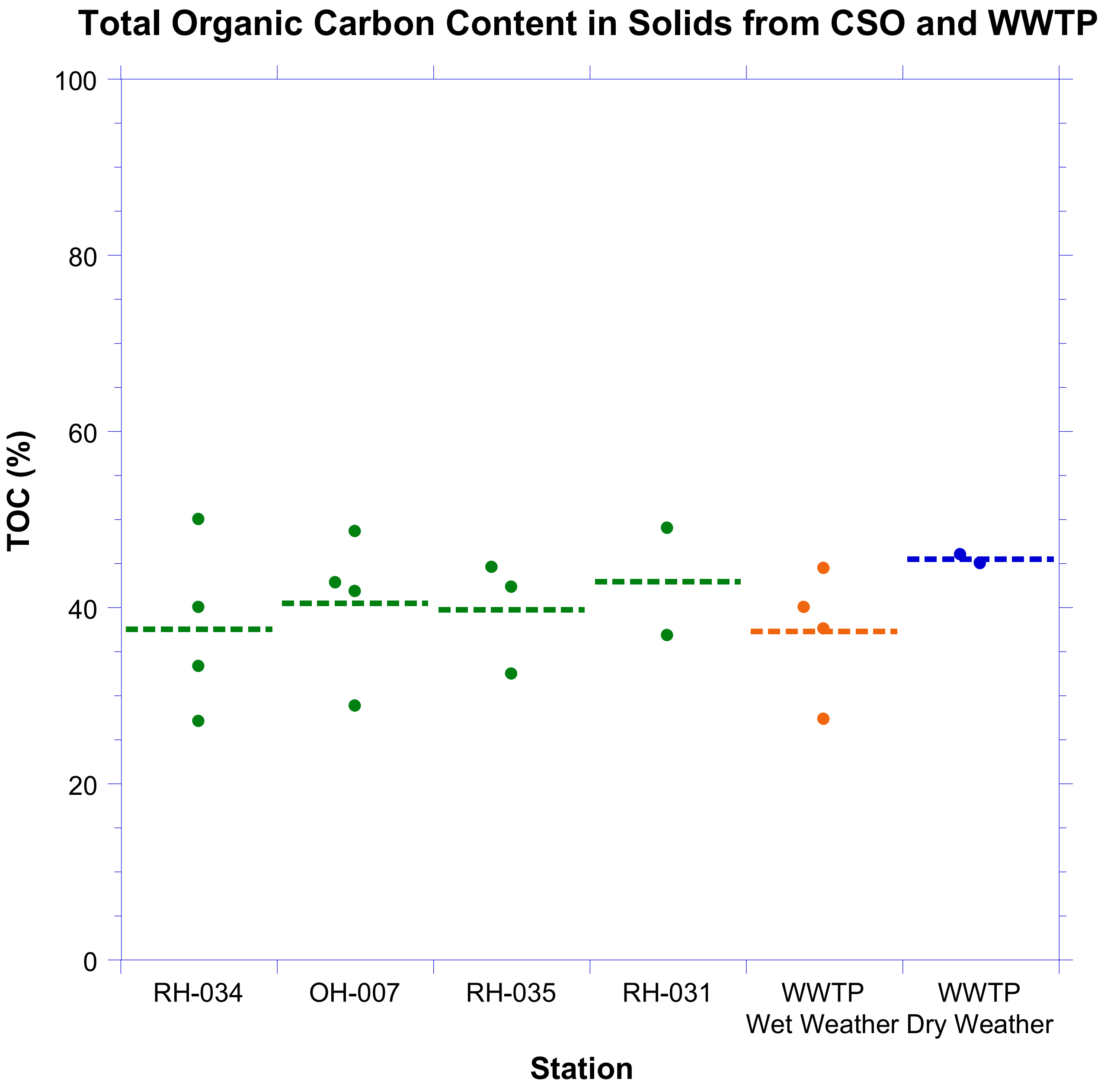

Percent Total Organic Carbon Content on Solids from CSO and WWTP

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Figure A1-4

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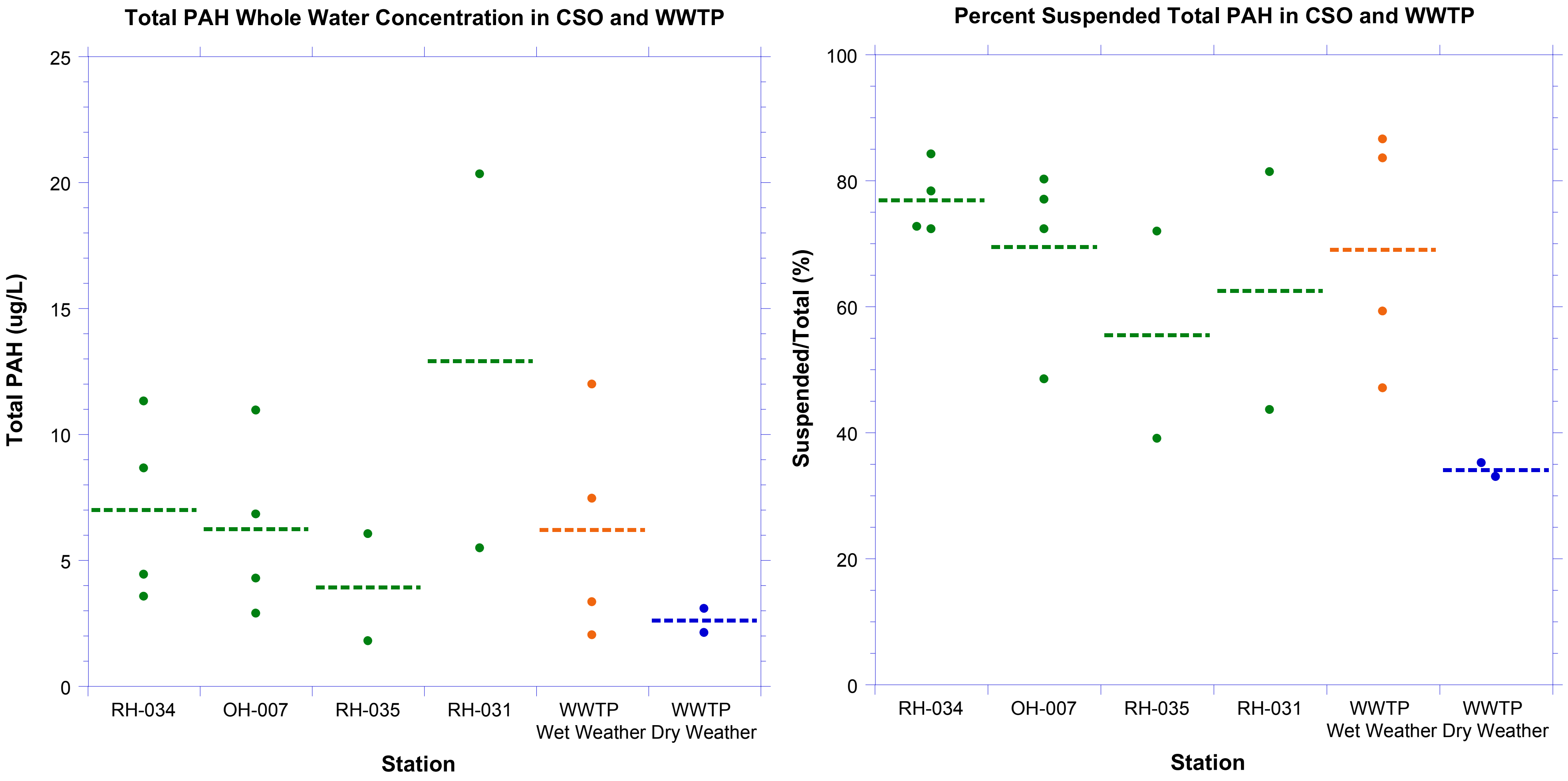

Total PAH Whole Water Concentration in CSO and WWTP

Percent Suspended Total PAH in CSO and WWTP

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Total PAH Concentration in CSO and WWTP

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Figure A1-5a

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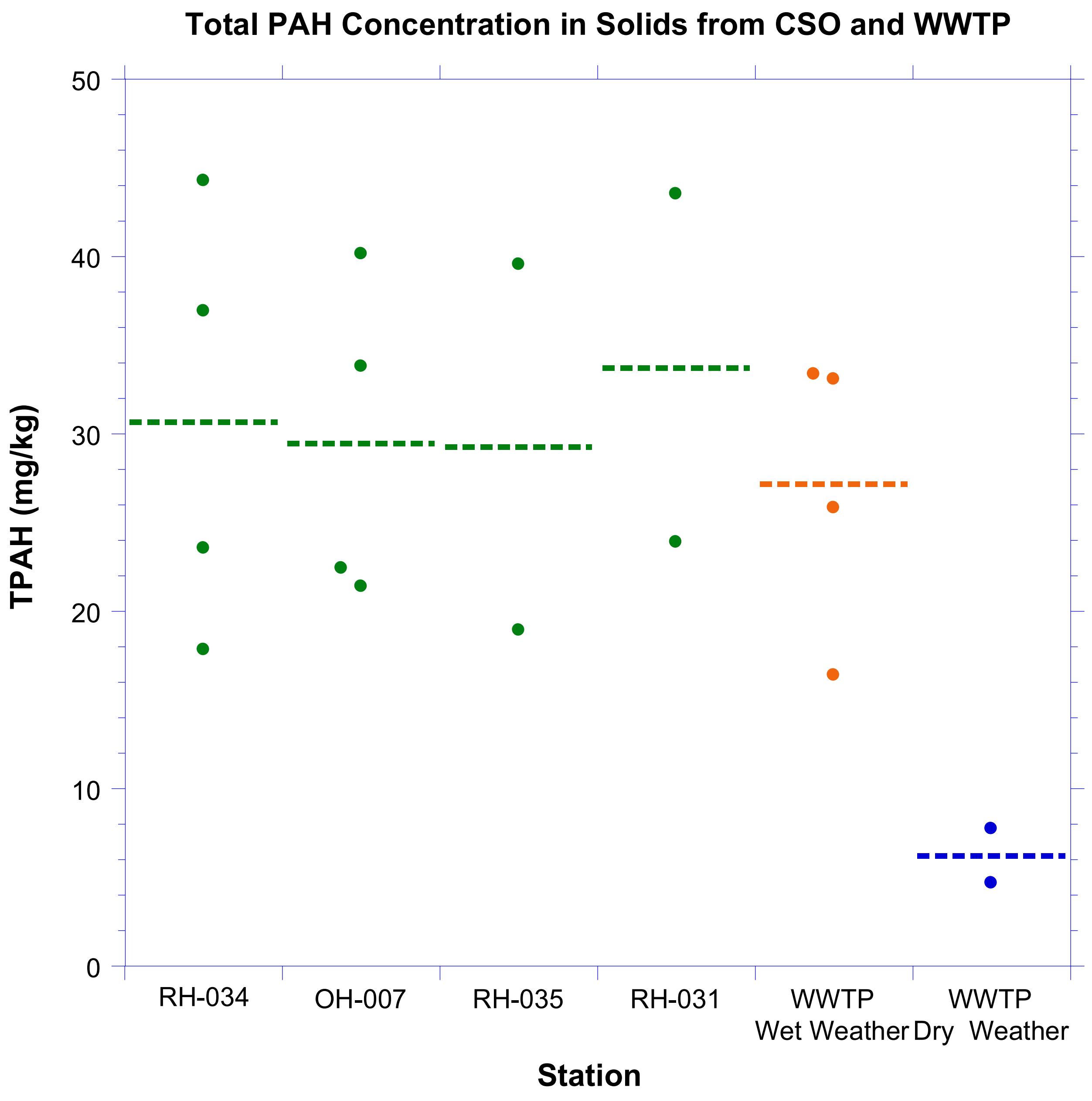

Total PAH Concentration on Solids from CSO and WWTP

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Figure A1-5b

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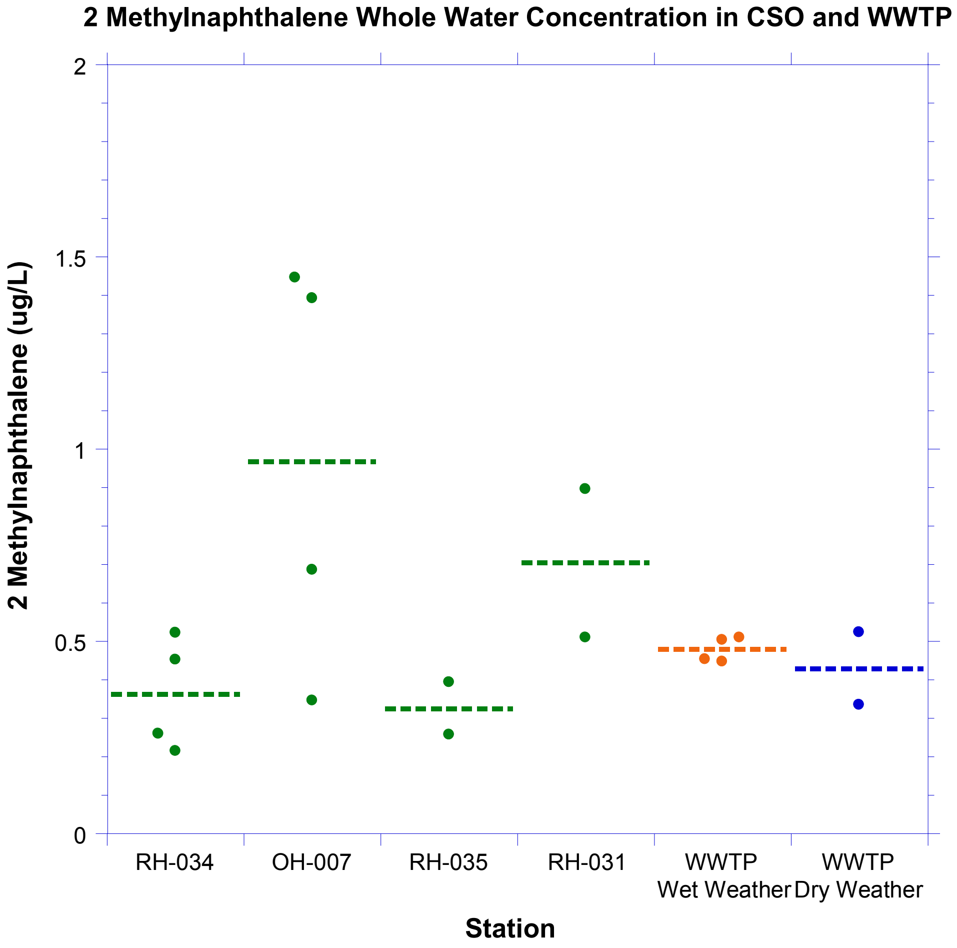

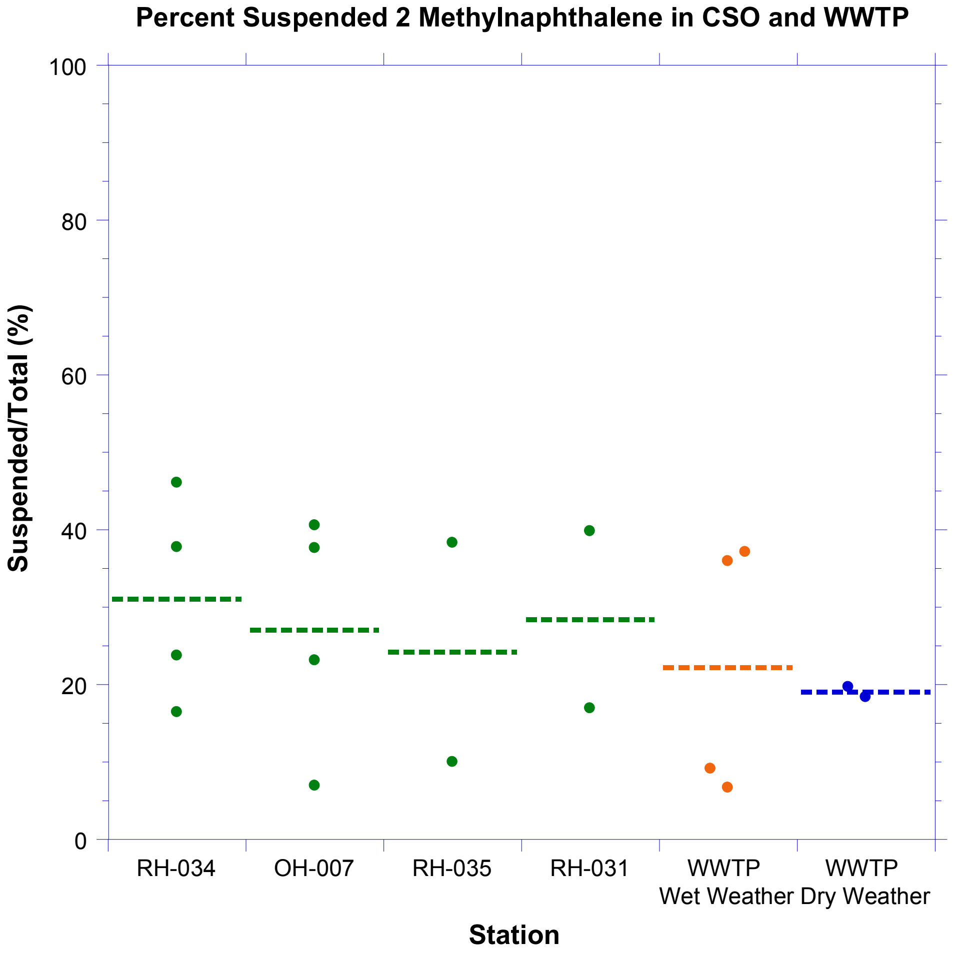

2 Methylnaphthalene Concentration in CSO and WWTP

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Figure A1-6a

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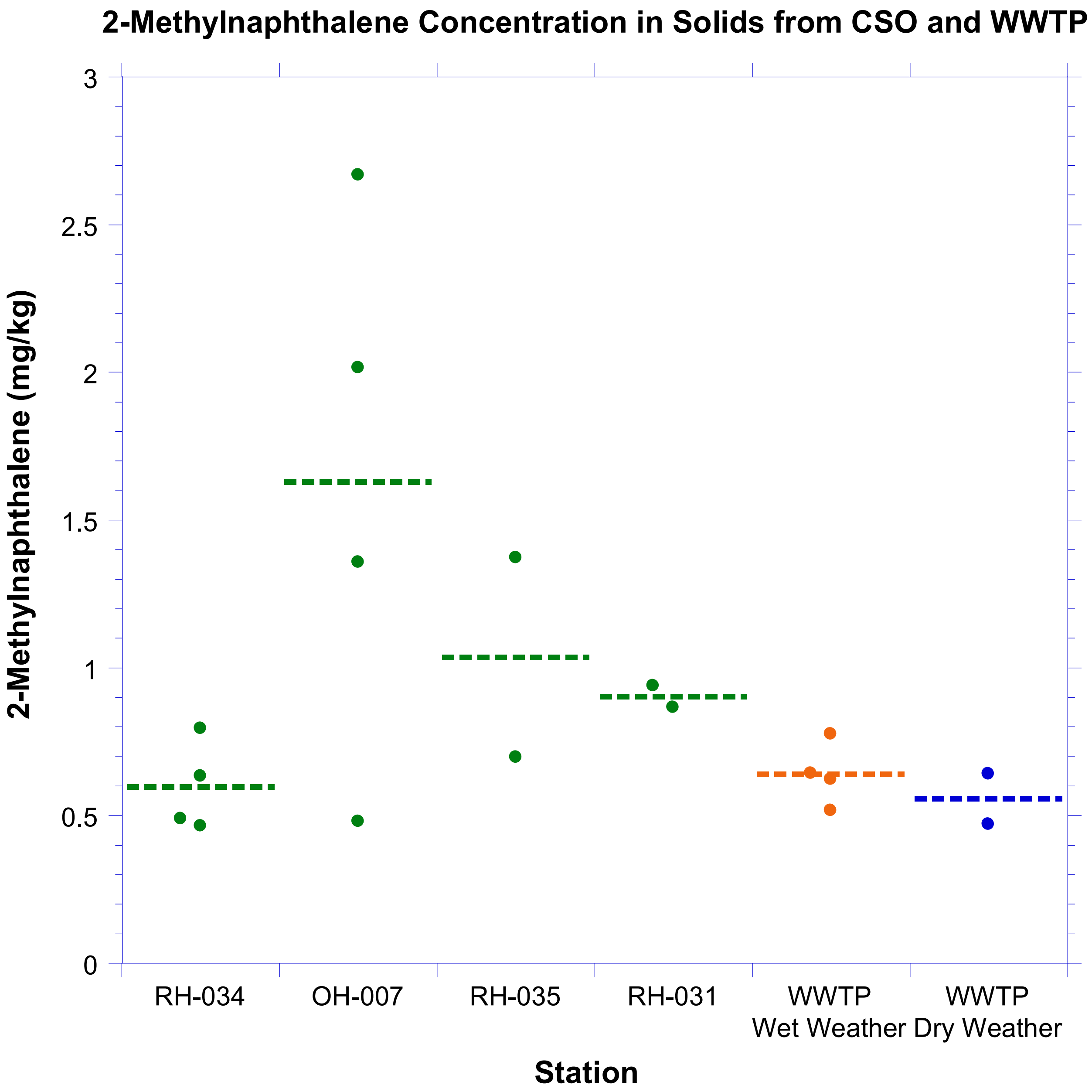
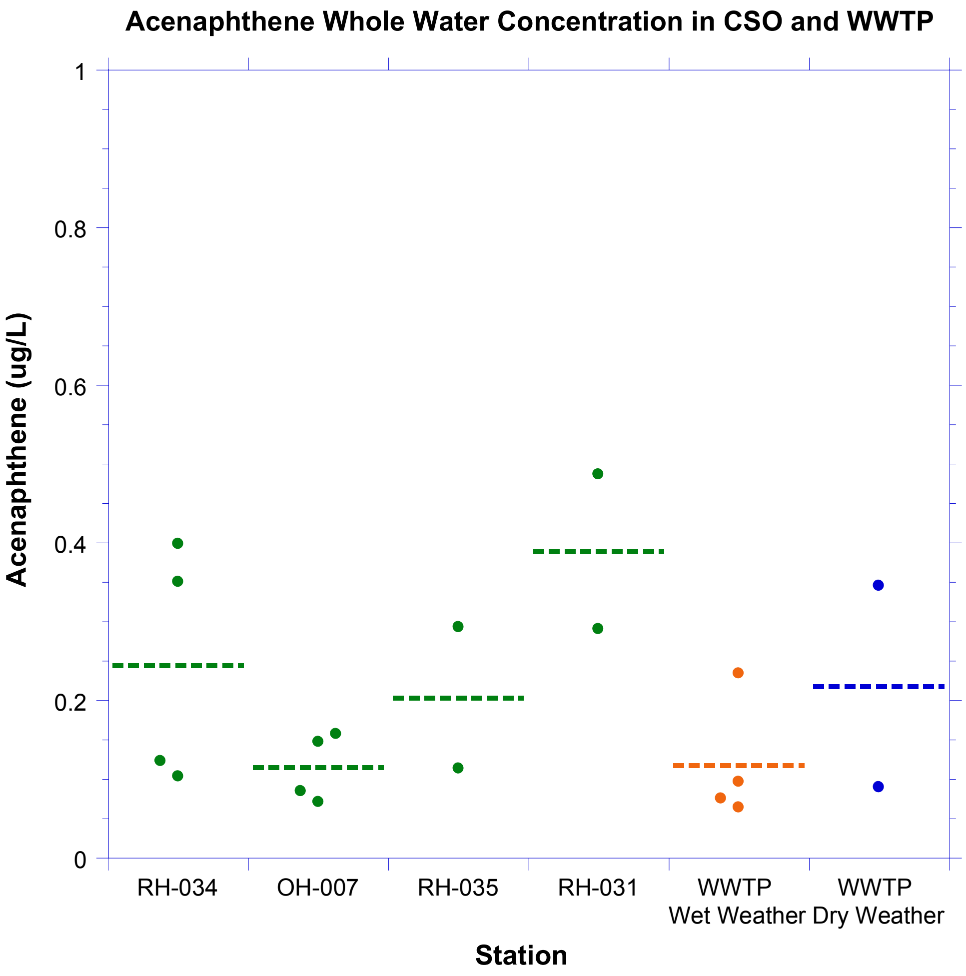


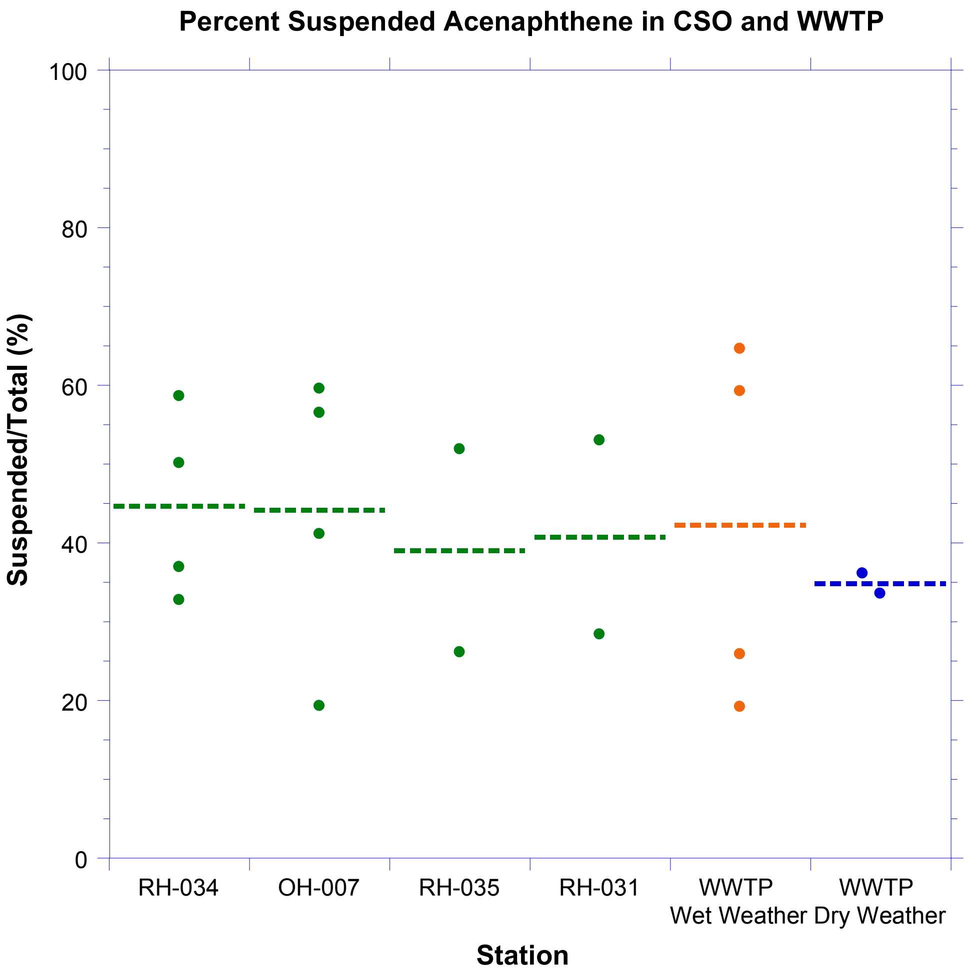
2 Methylnaphthalene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-6b

April 2013





Acenaphthene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-7a

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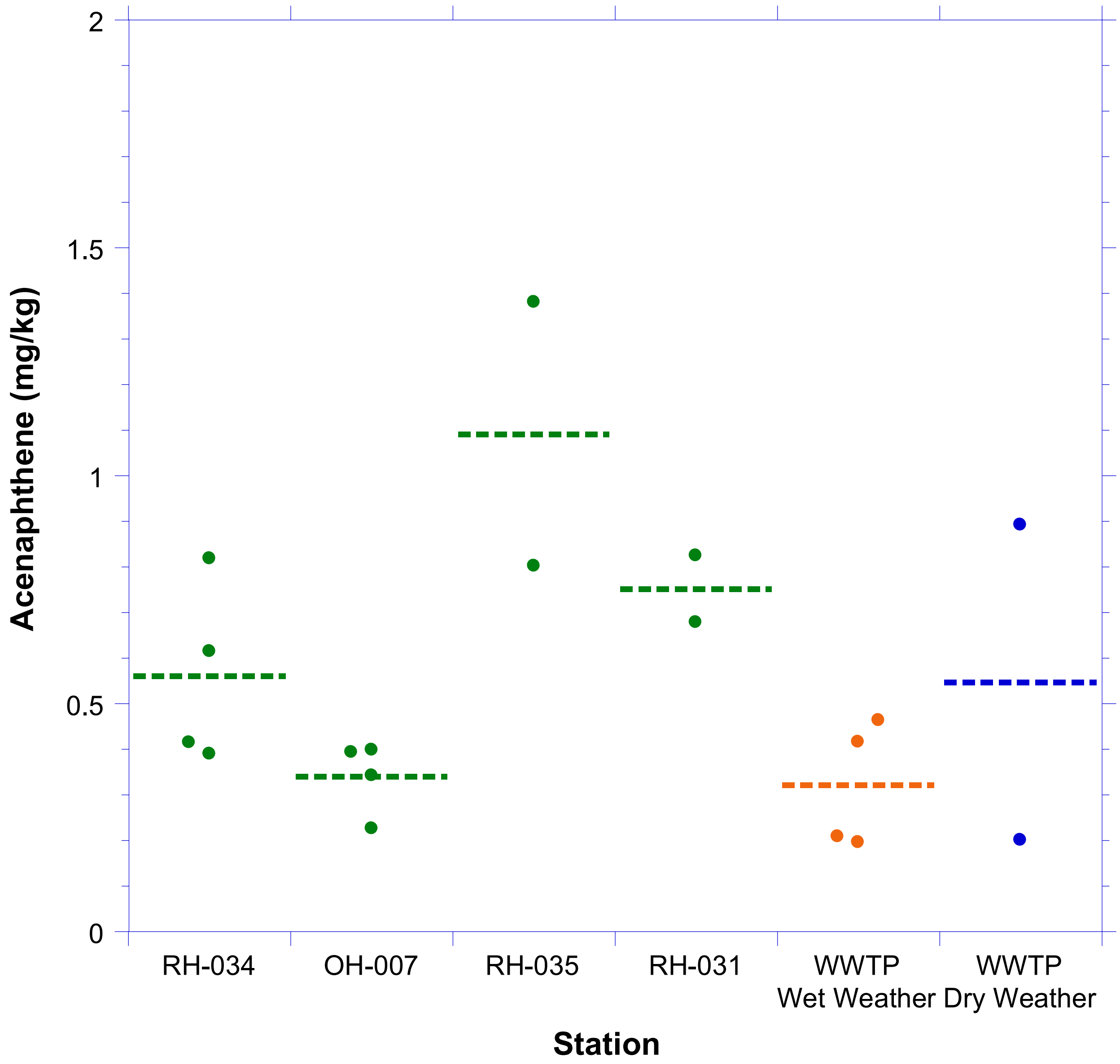
Acenaphthene Concentration in Solids from CSO and WWTP



Acenaphthene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-7b

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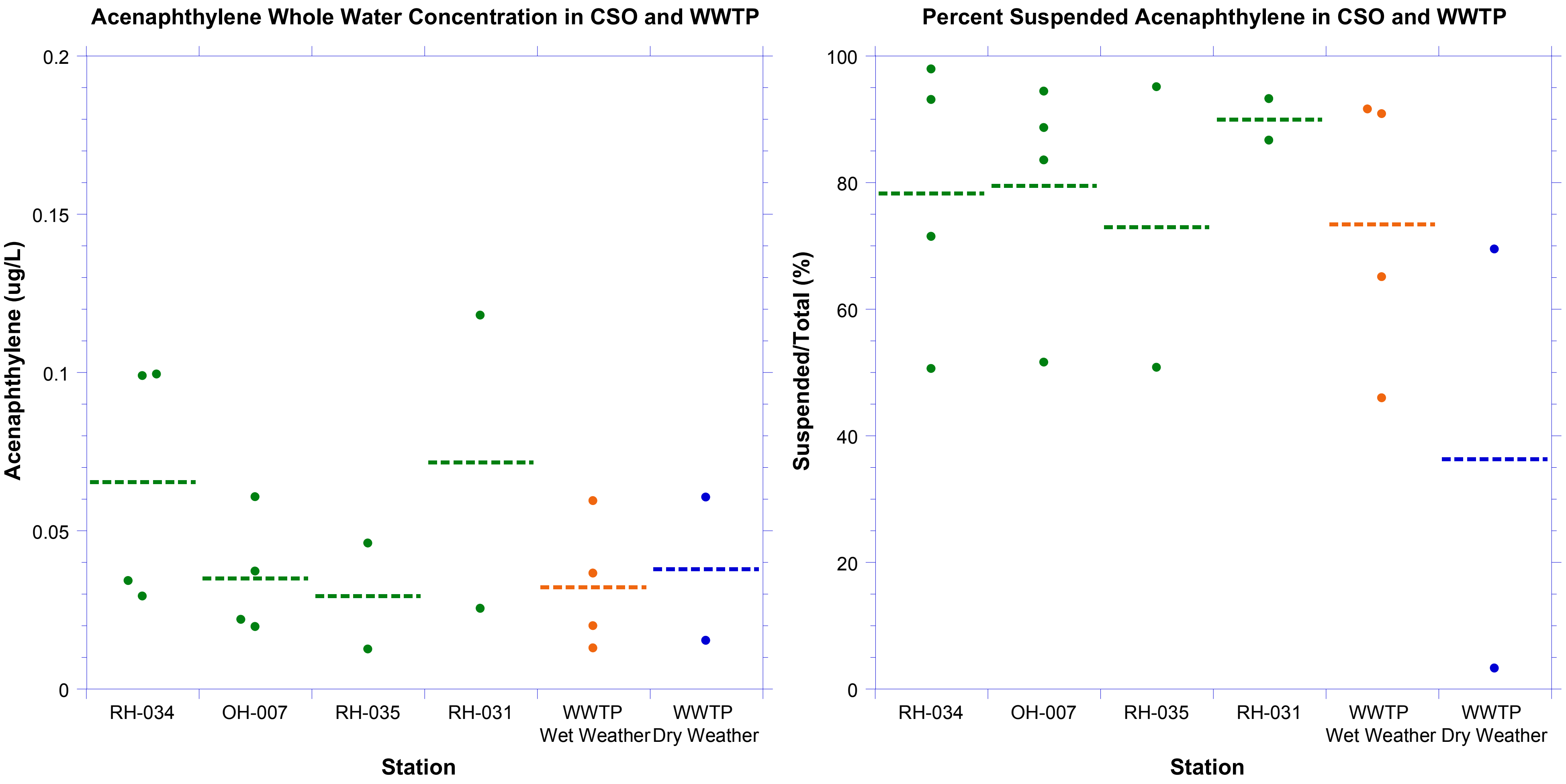
Acenaphthylene Whole Water Concentration in CSO and WWTP

Percent Suspended Acenaphthylene in CSO and WWTP

Acenaphthylene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-8a

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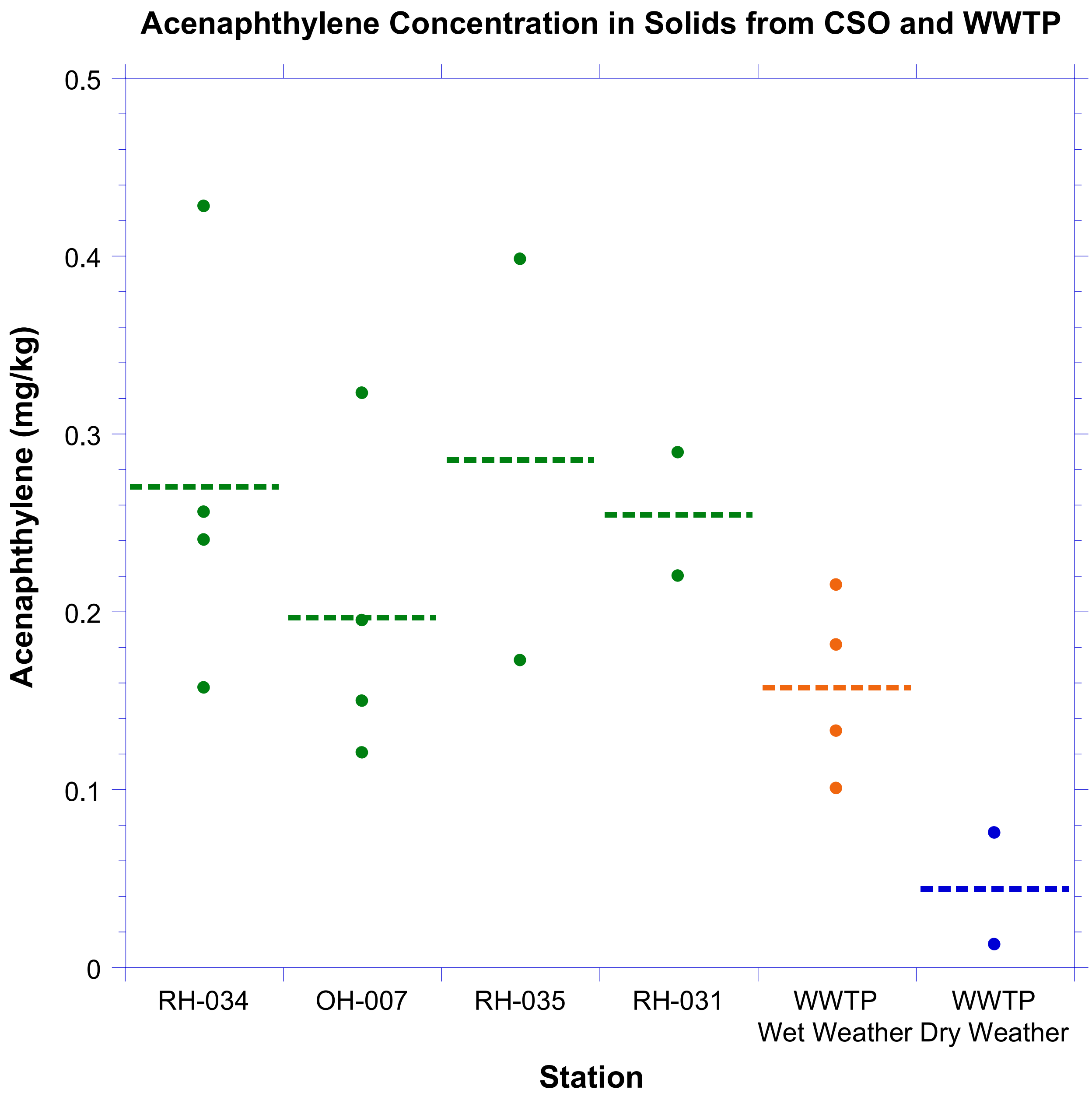
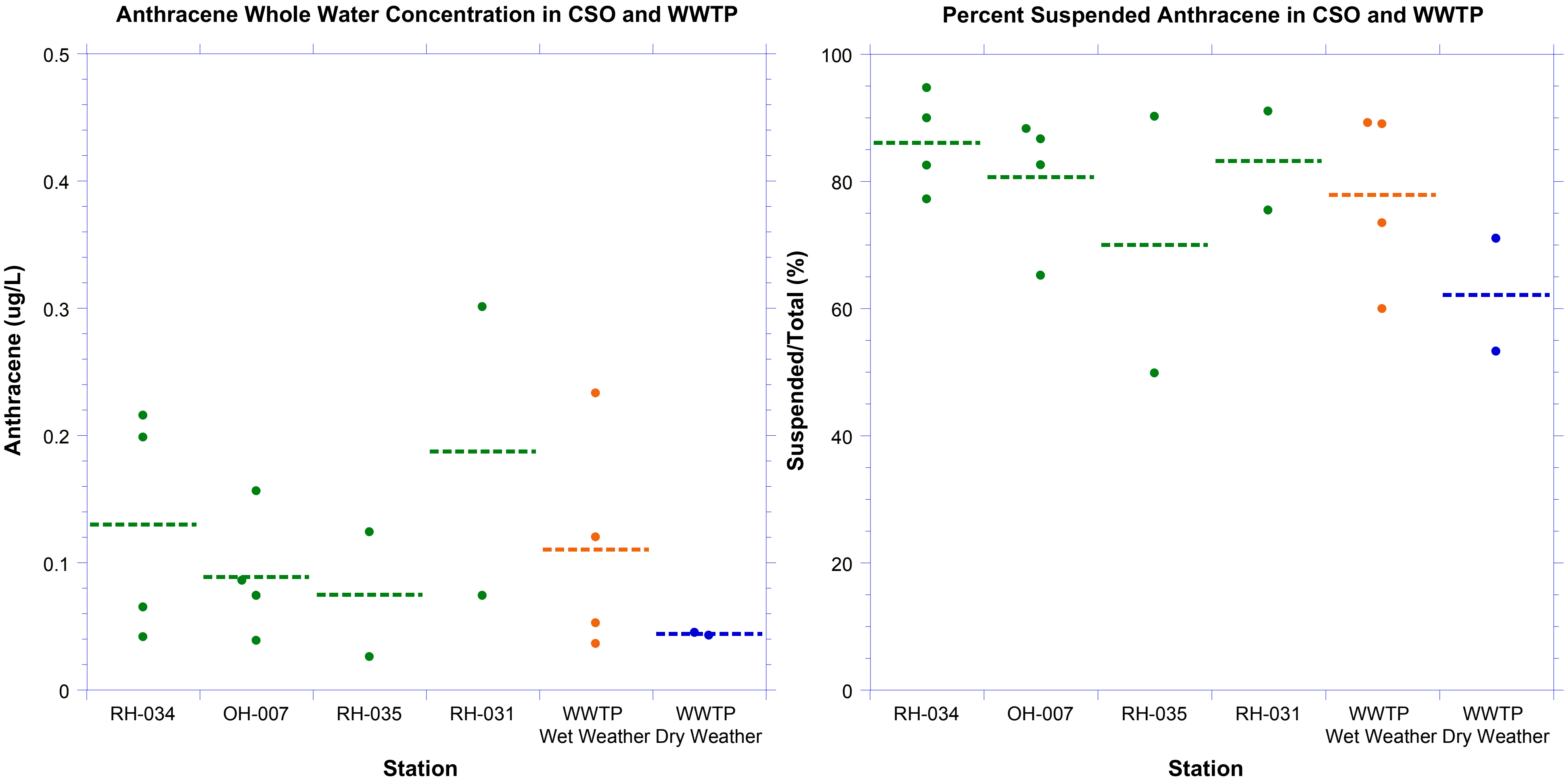


Acenaphthylene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-8b

April 2013



Anthracene Concentration in CSO and WWTP

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Figure A1-9a

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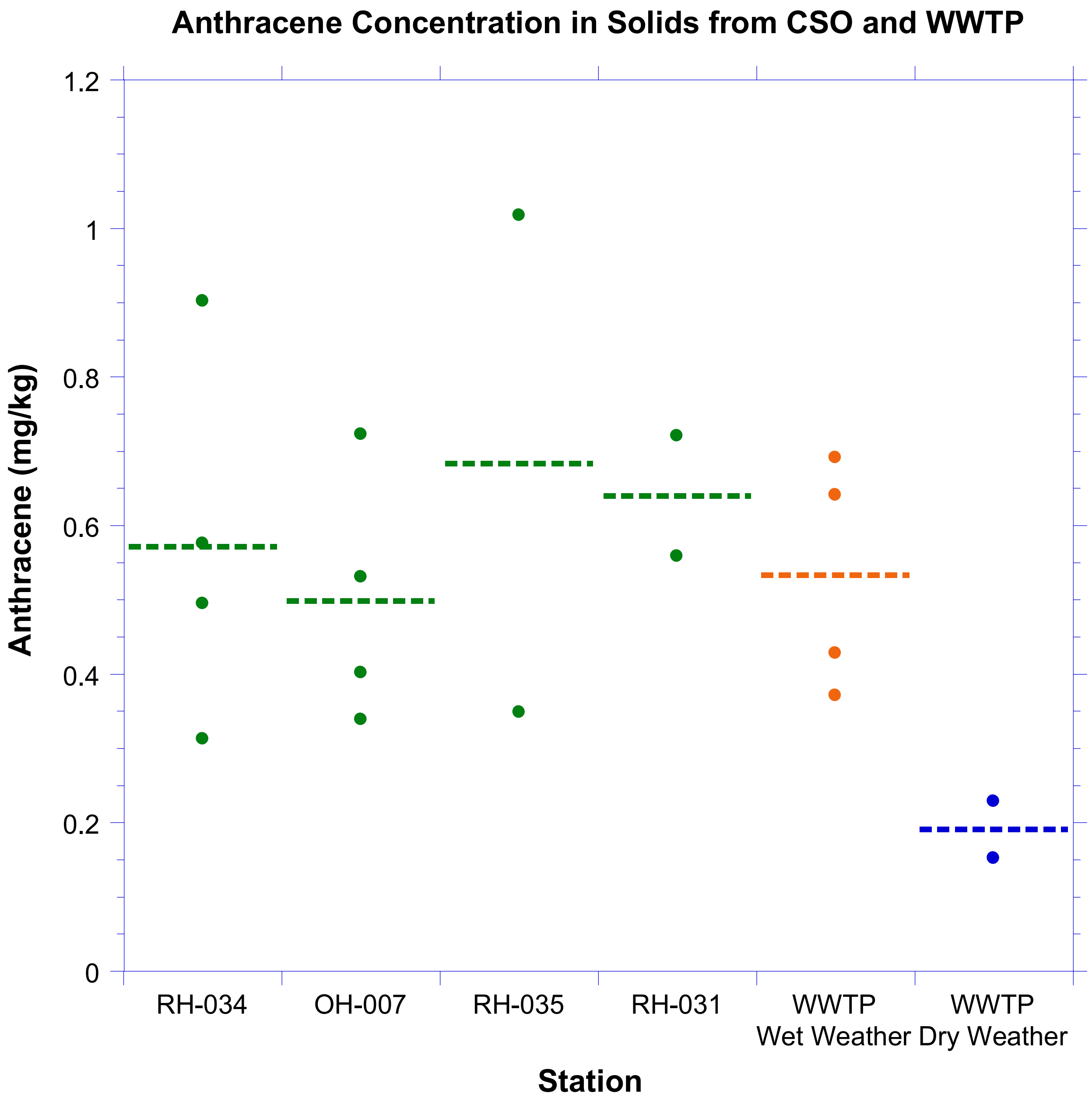

Anthracene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-9b

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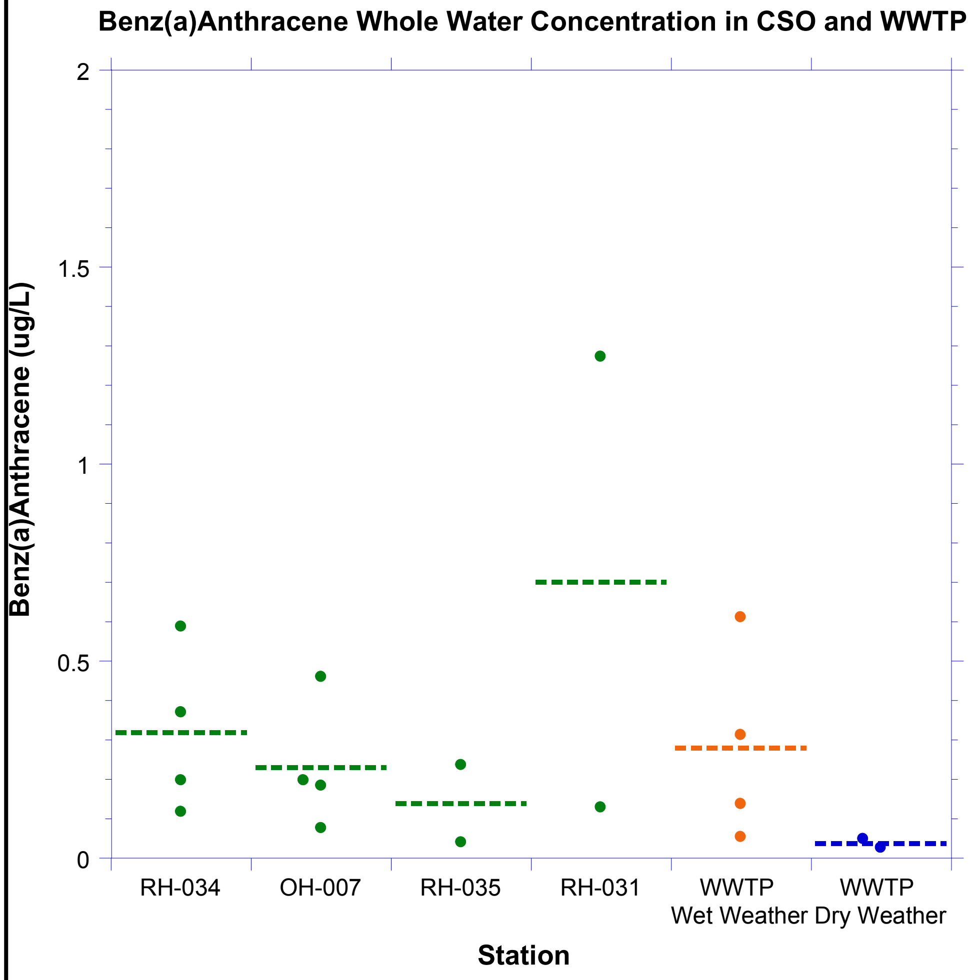

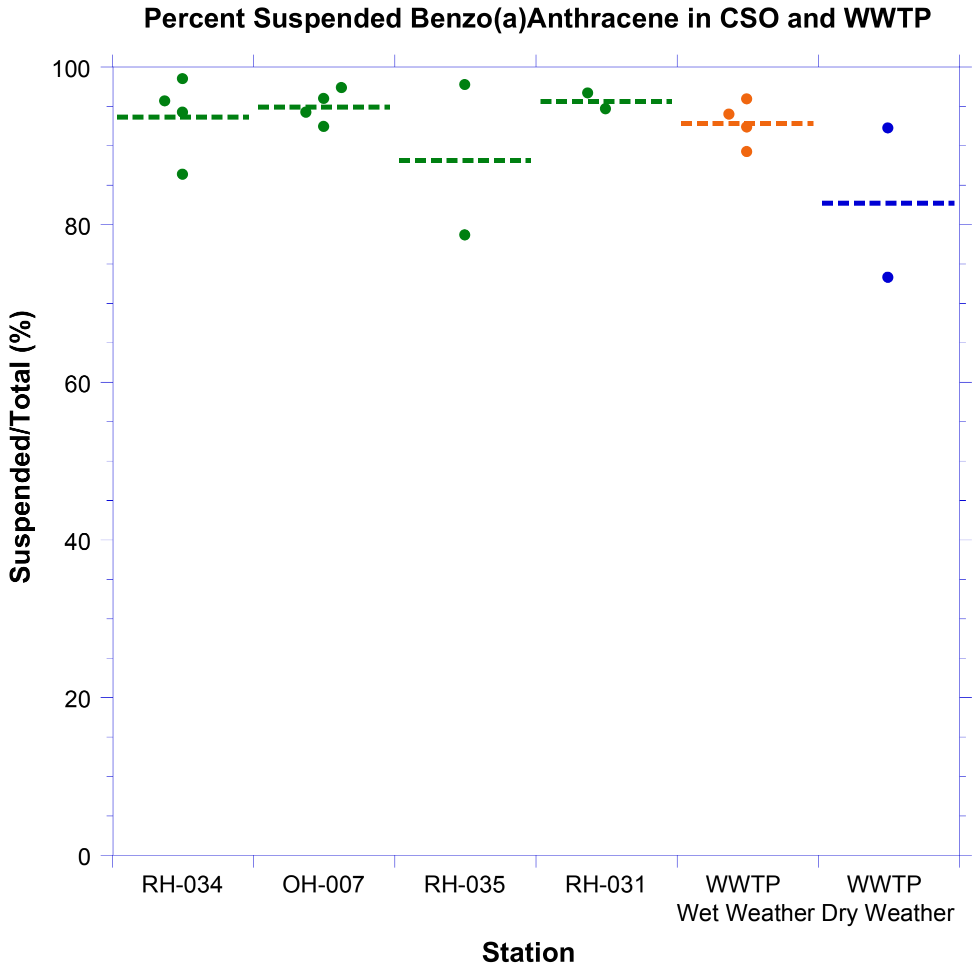

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Benz(a)Anthracene Concentration in CSO and WWTP

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Figure A1-10a

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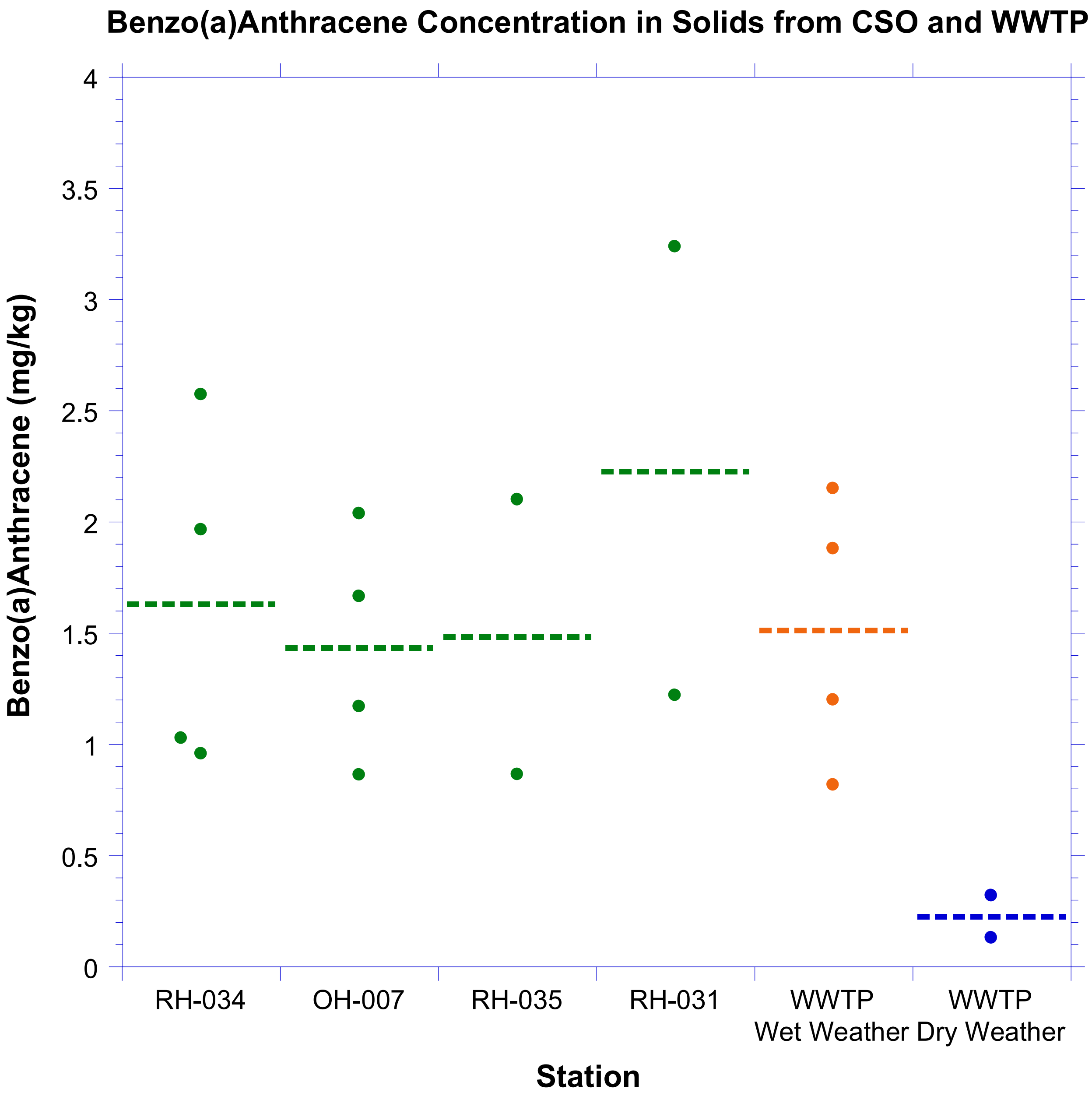

Benz(a)Anthracene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-10b

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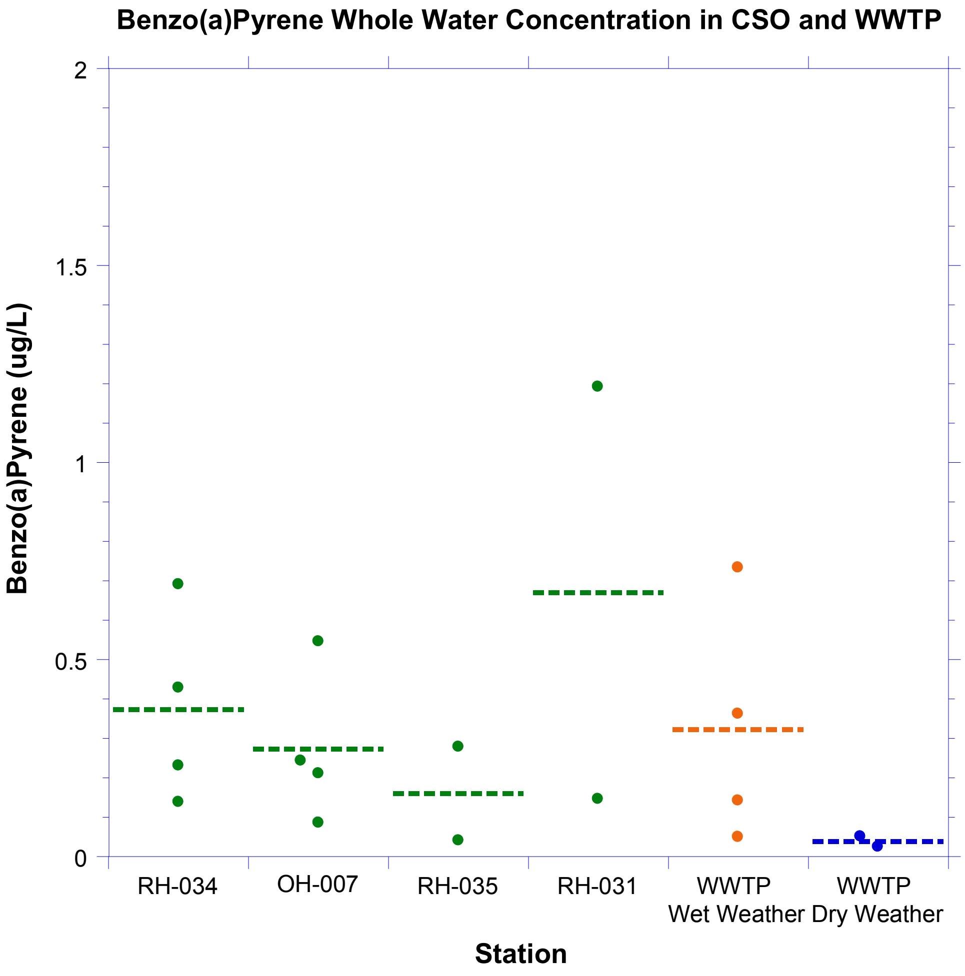

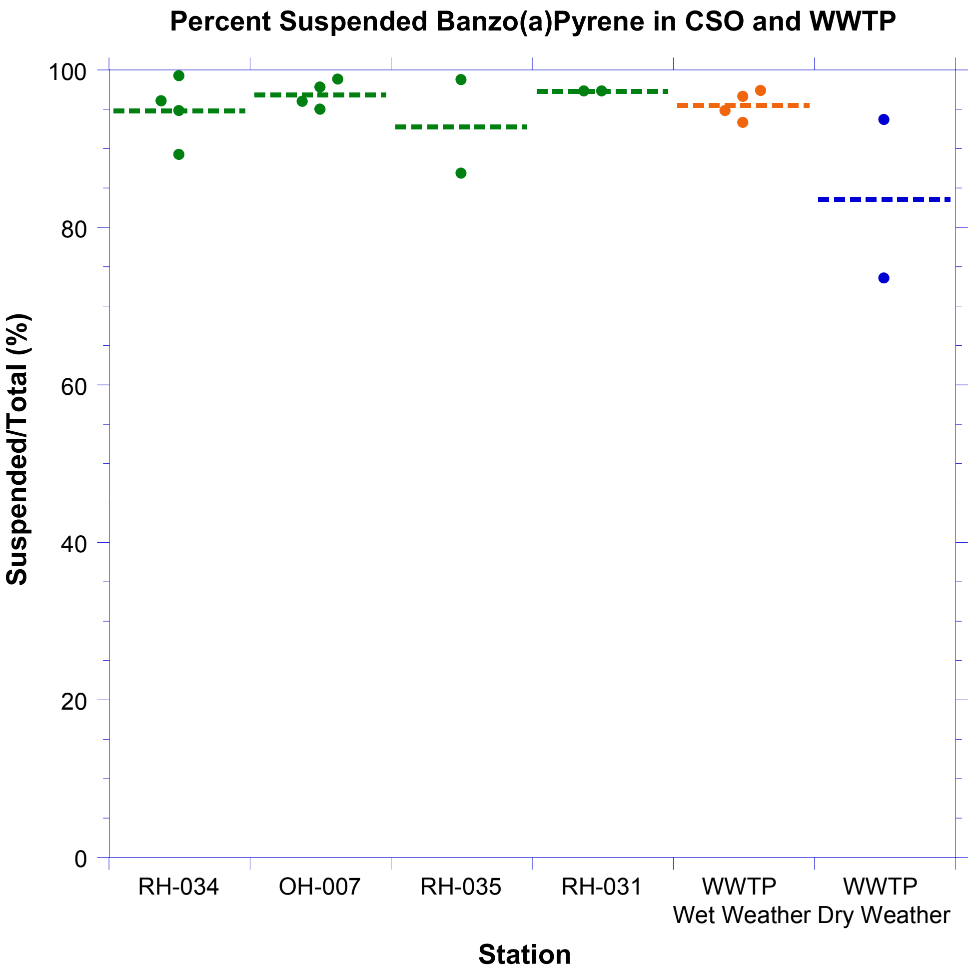

Benzo(a)Pyrene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-11a

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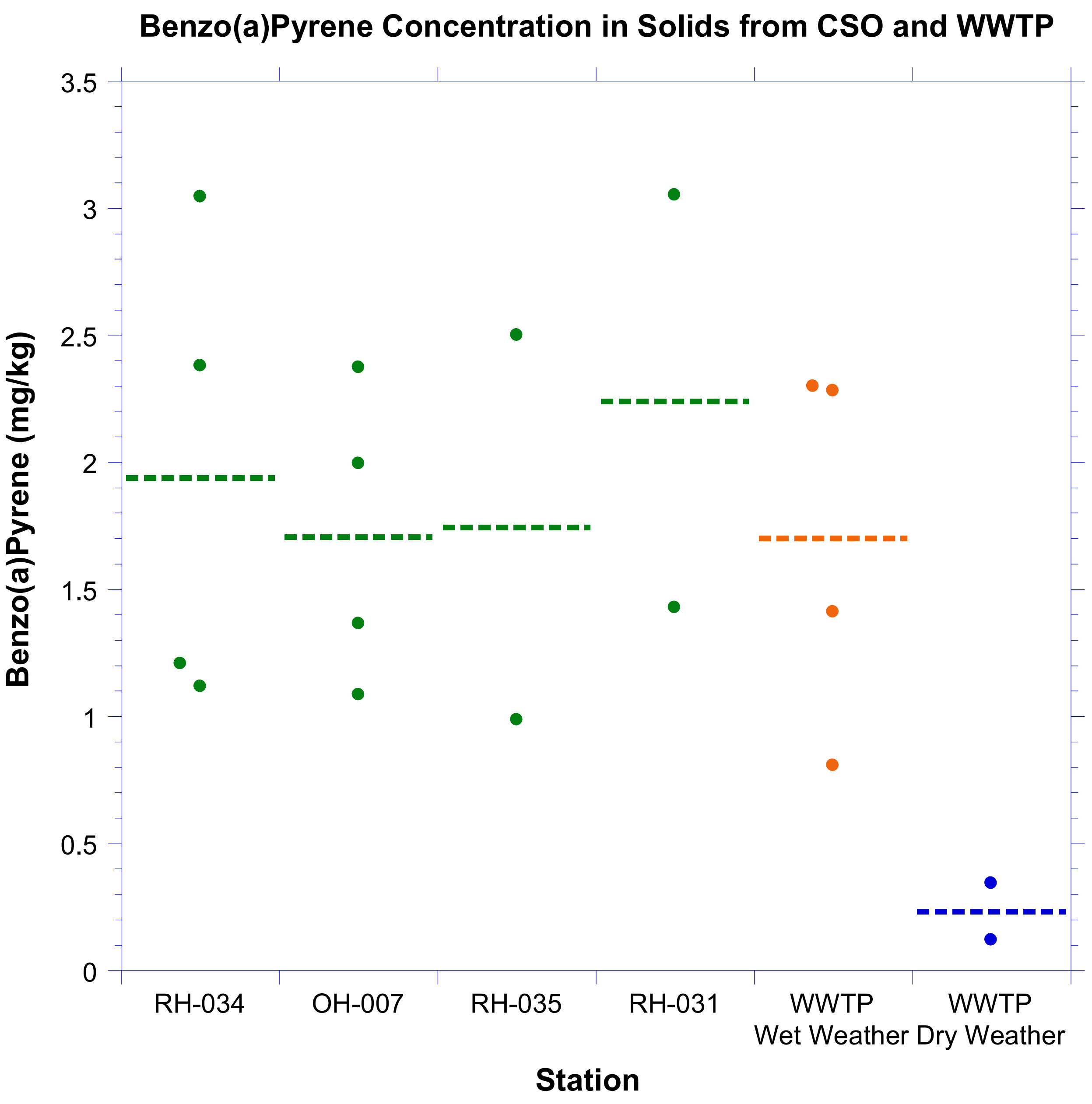
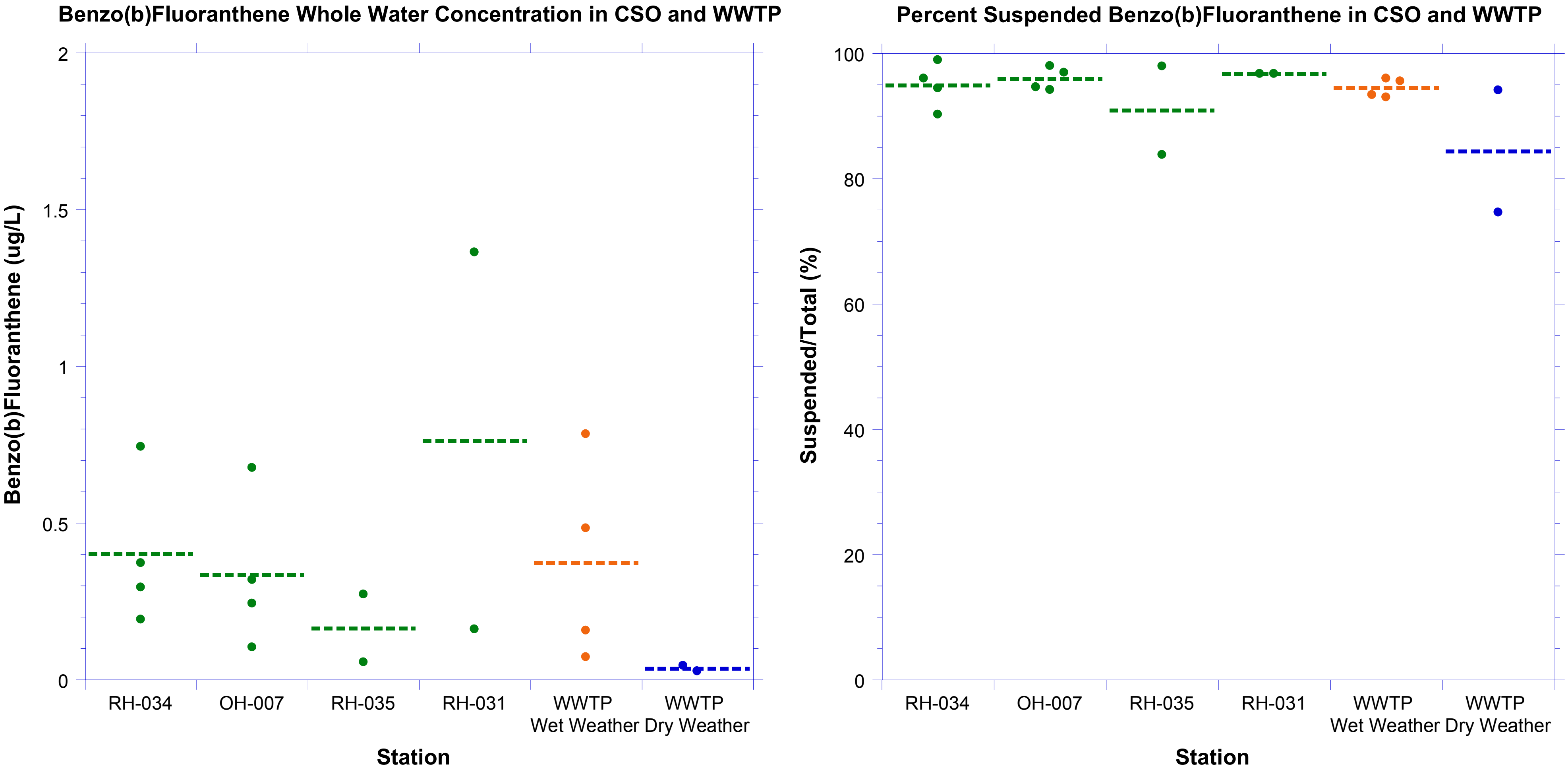


Benzo(a)Pyrene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-11b

April 2013


Benzo(b)Fluoranthene Whole Water Concentration in CSO and WWTP

Percent Suspended Benzo(b)Fluoranthene in CSO and WWTP

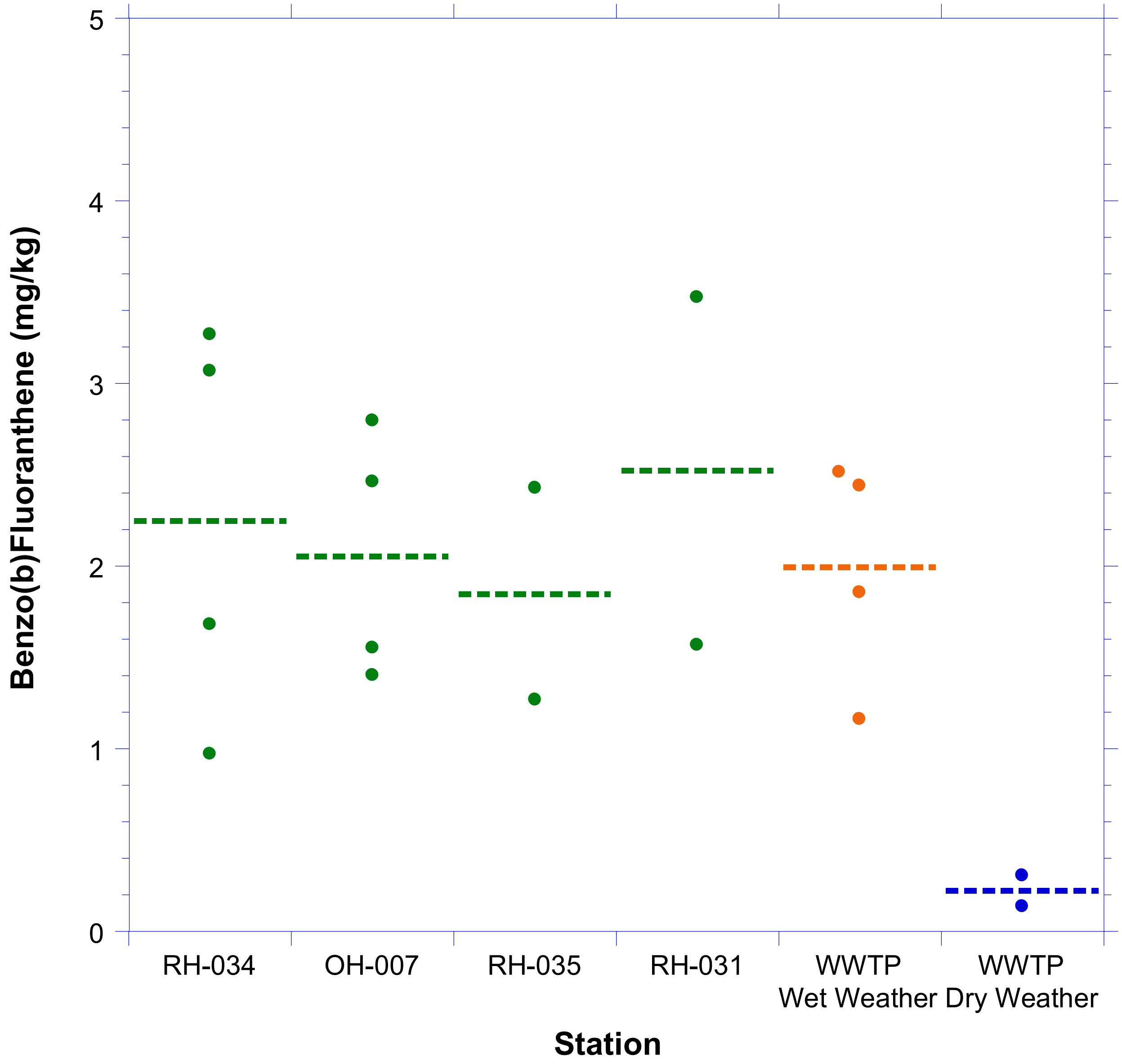
Benzo(b)Fluoranthene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-12a

April 2013

Benzo(b)Fluoranthene Concentration in Solids from CSO and WWTP



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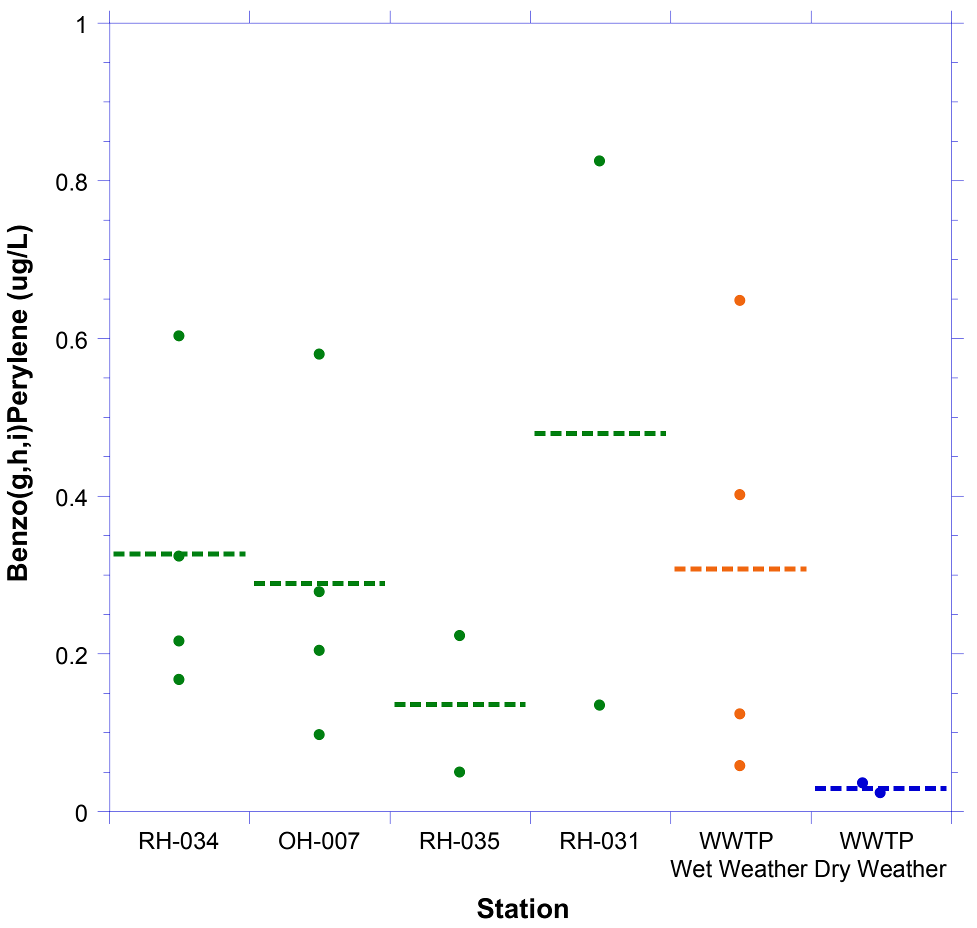
Benzo(b)Fluoranthene Concentration on Solids from CSO and WWTP

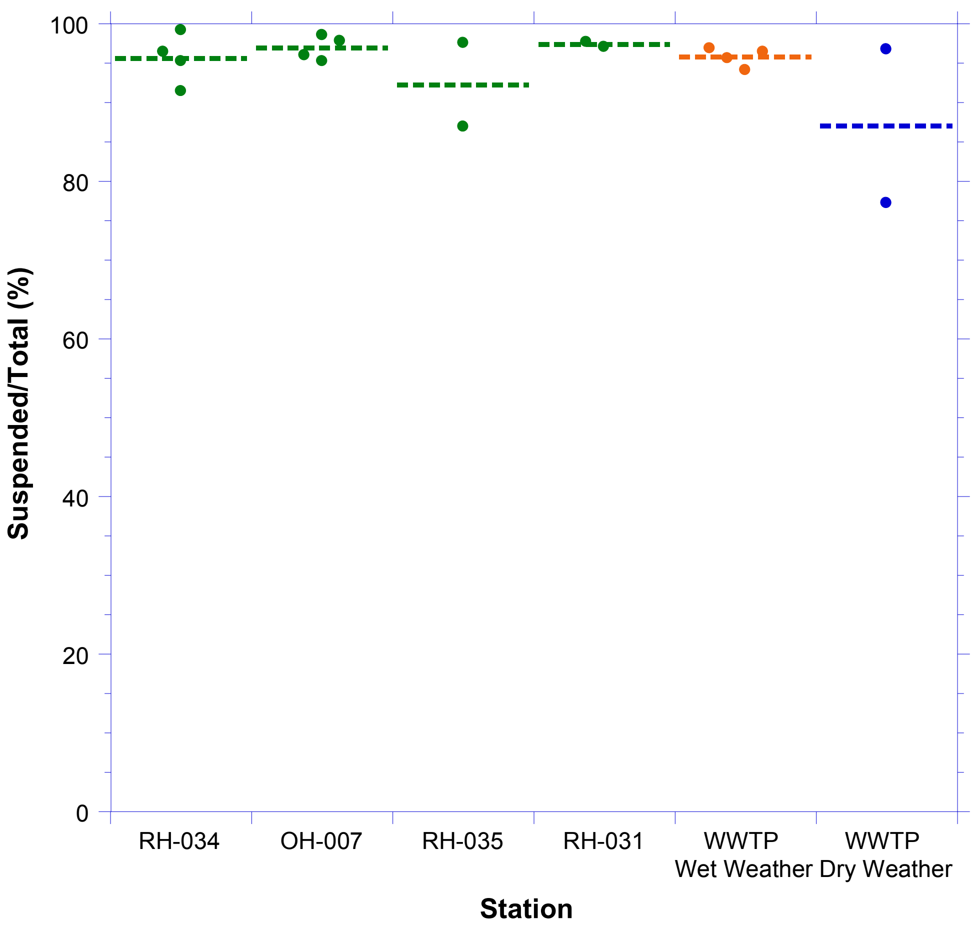
Gowanus Canal Superfund Site

Figure A1-12b

April 2013



Benzo(g,h,i)Perylene Whole Water Concentration in CSO and WWTP



Percent Suspended Benzo(g,h,i)Perylene in CSO and WWTP

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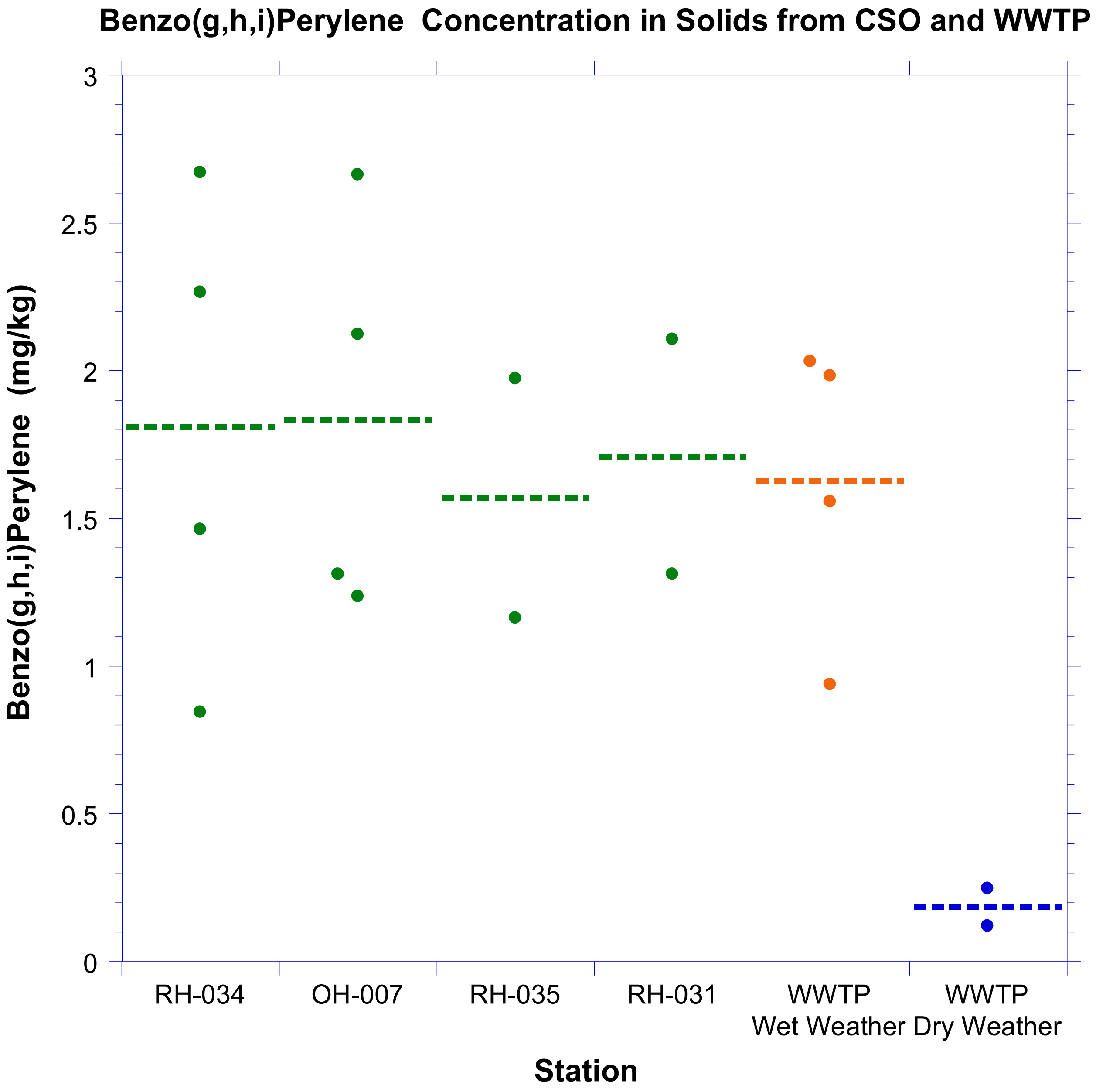
Benzo(g,h,i)Perylene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-13a

April 2013



Benzo(g,h,i)Perylene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-13b

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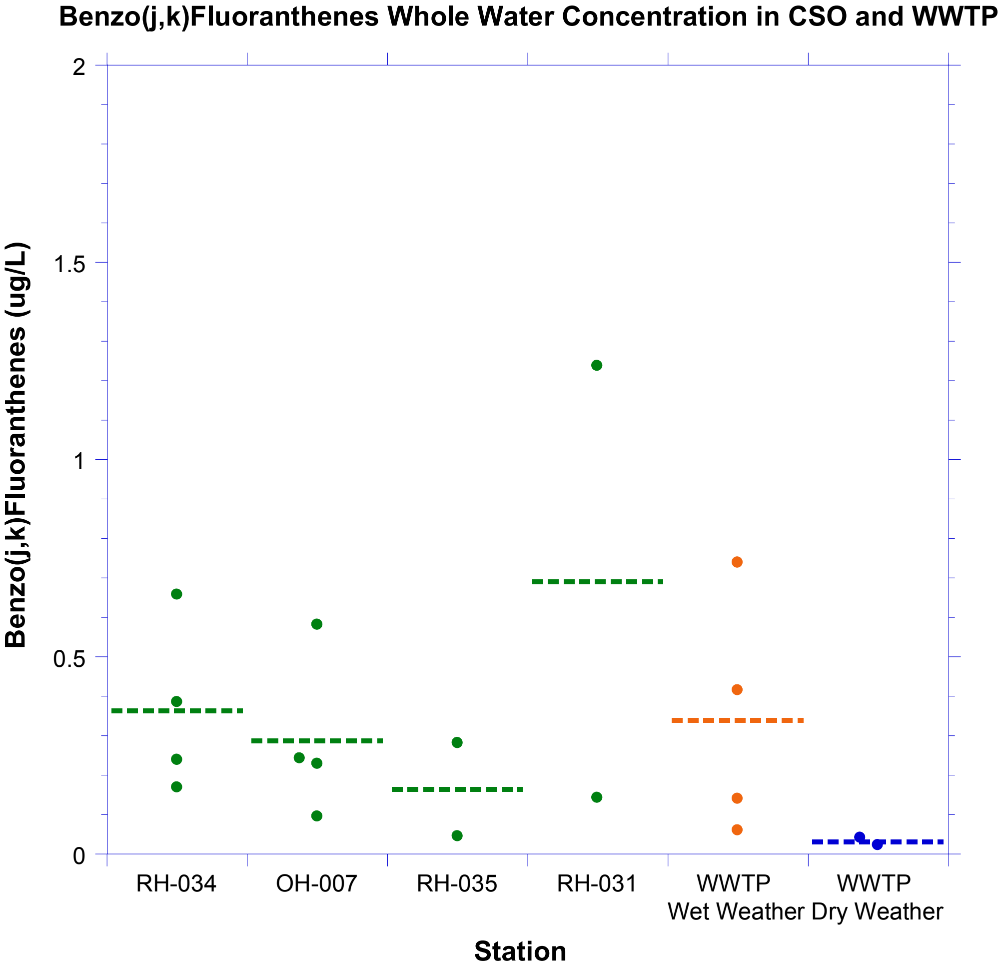

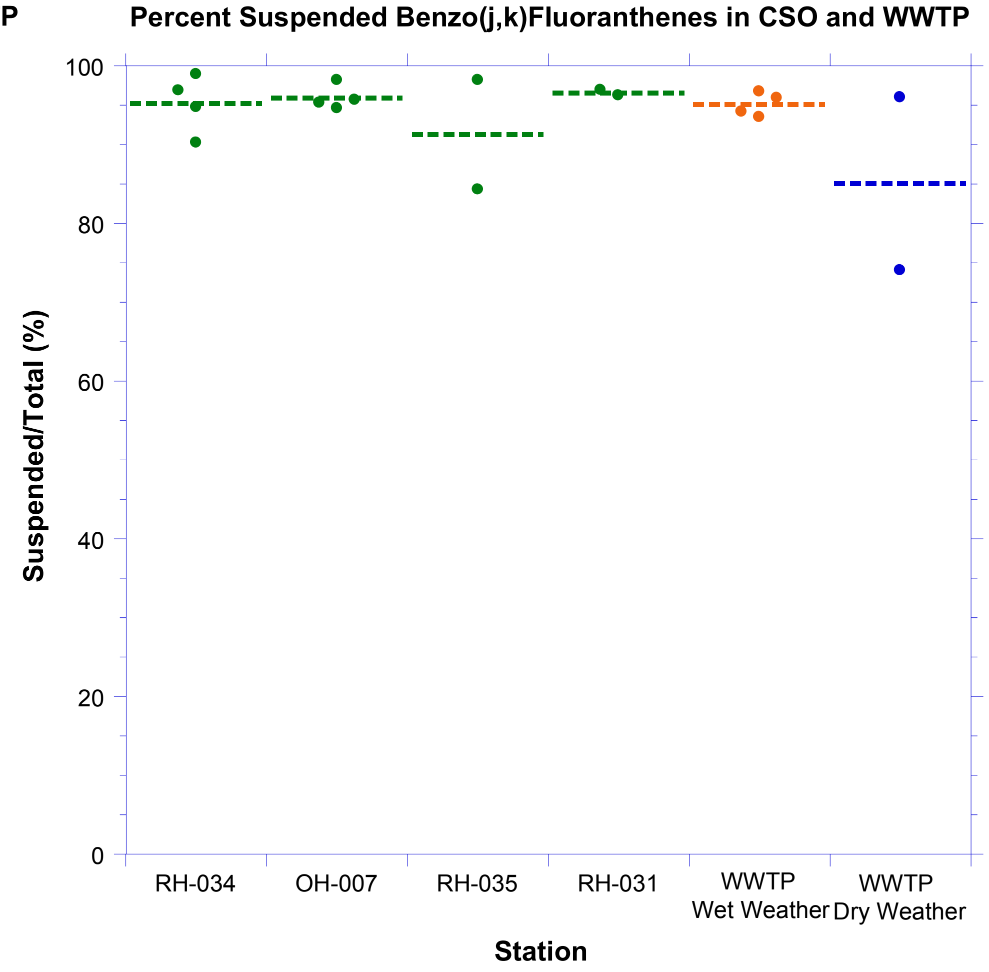

NYC Environmental Protection

Benzo(j,k)Fluoranthenes Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-14a

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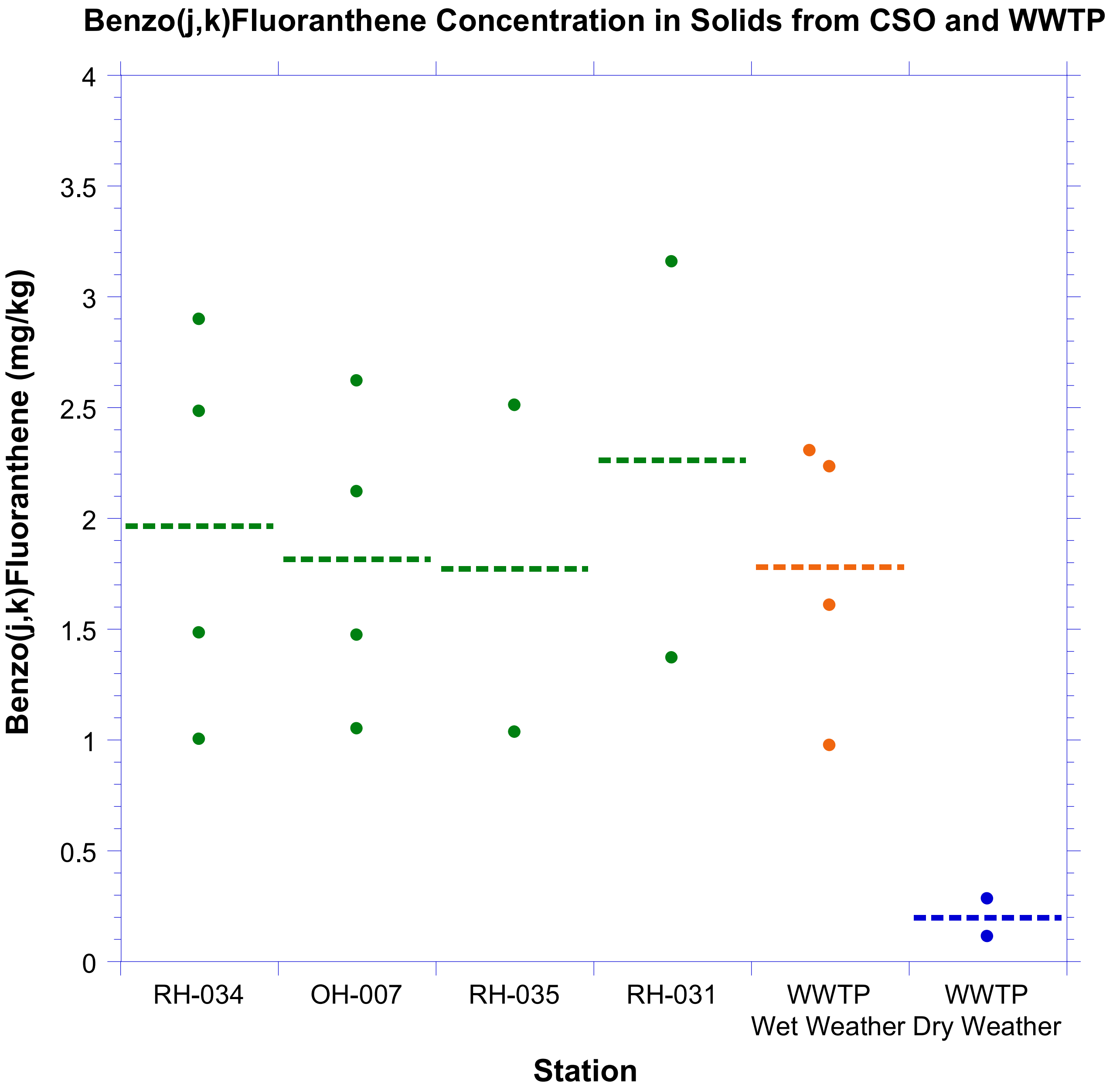
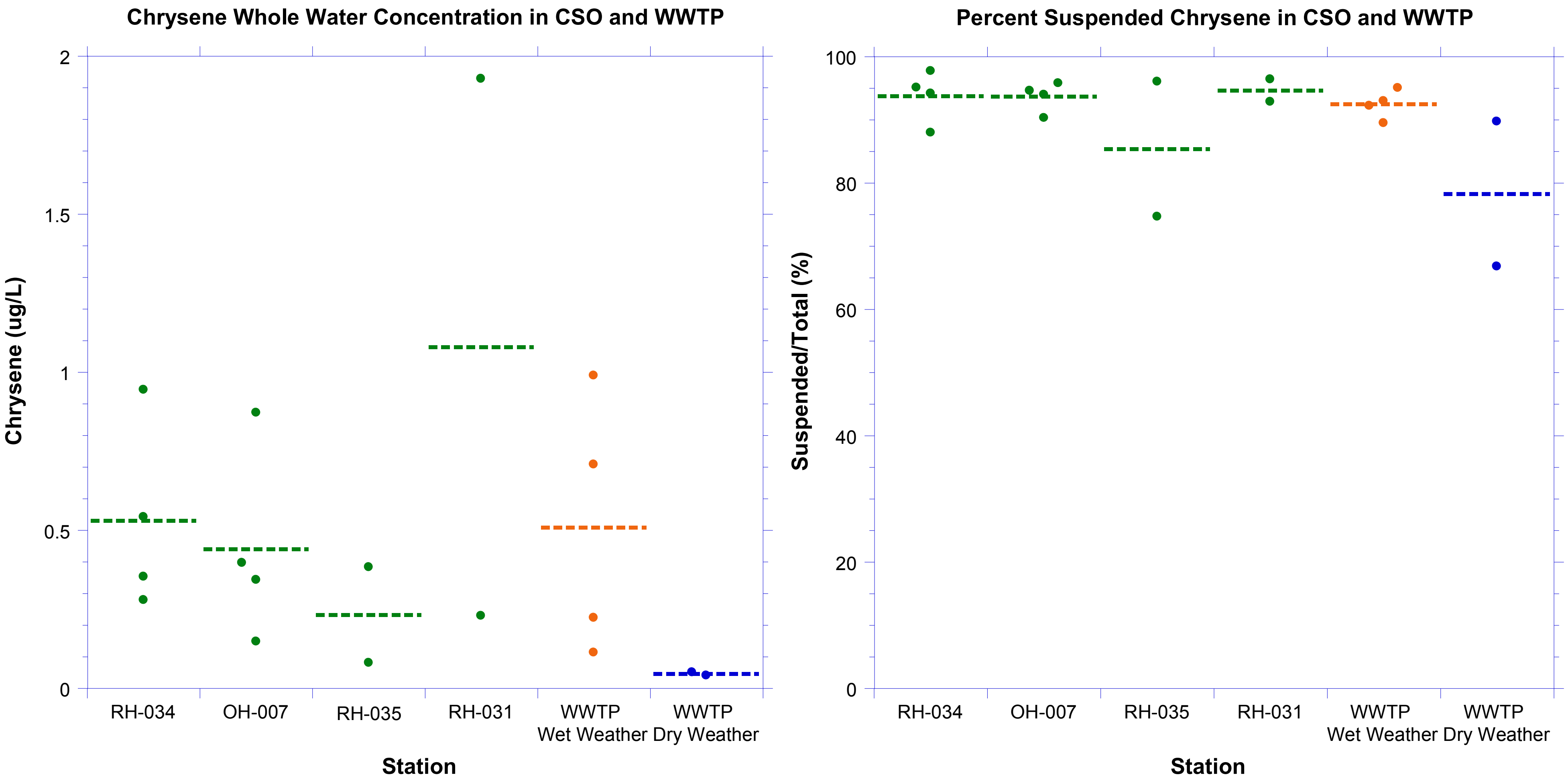


Benzo(j,k)Fluoranthenes Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-14b

April 2013

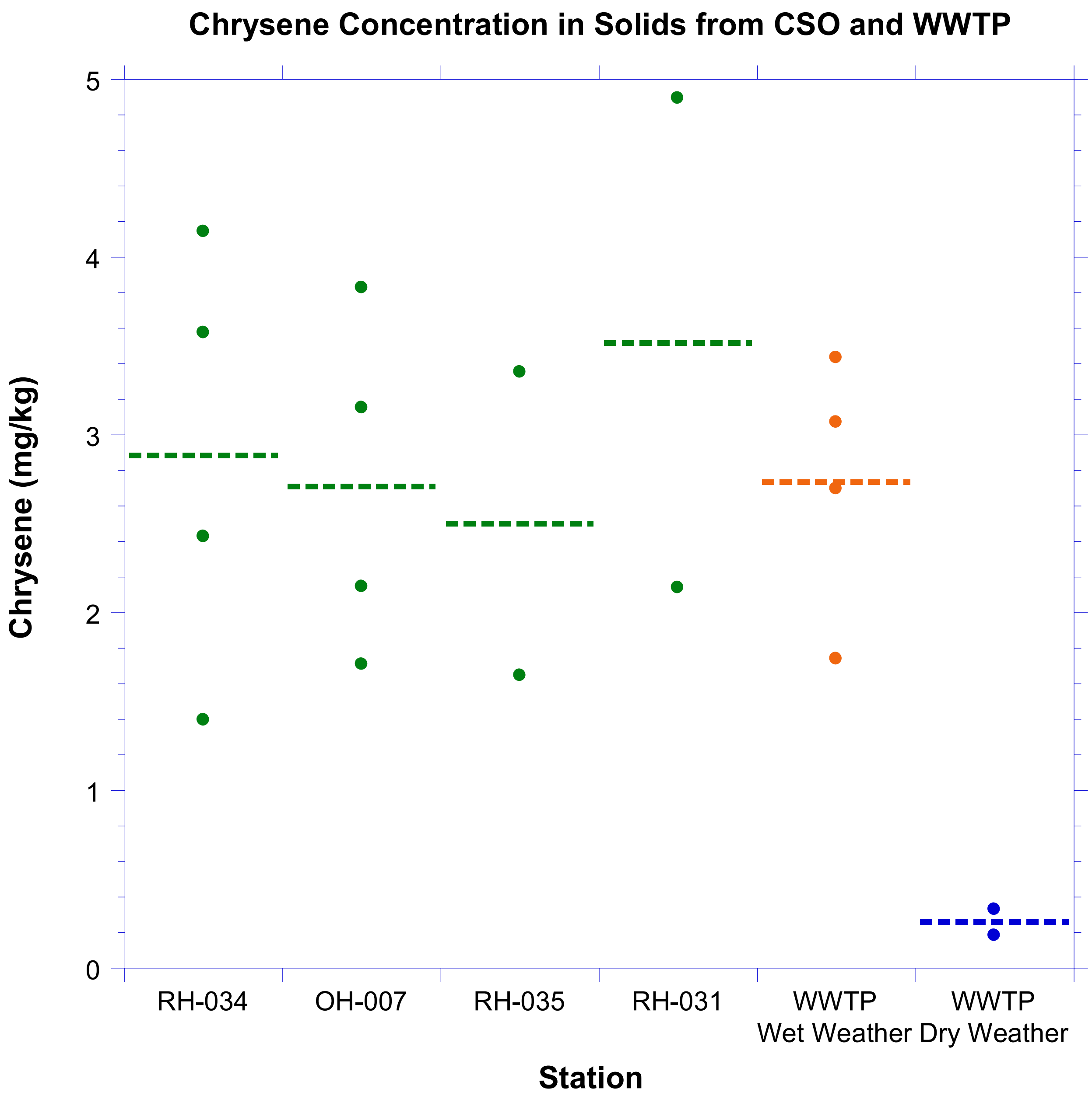


Chrysene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-15a

April 2013

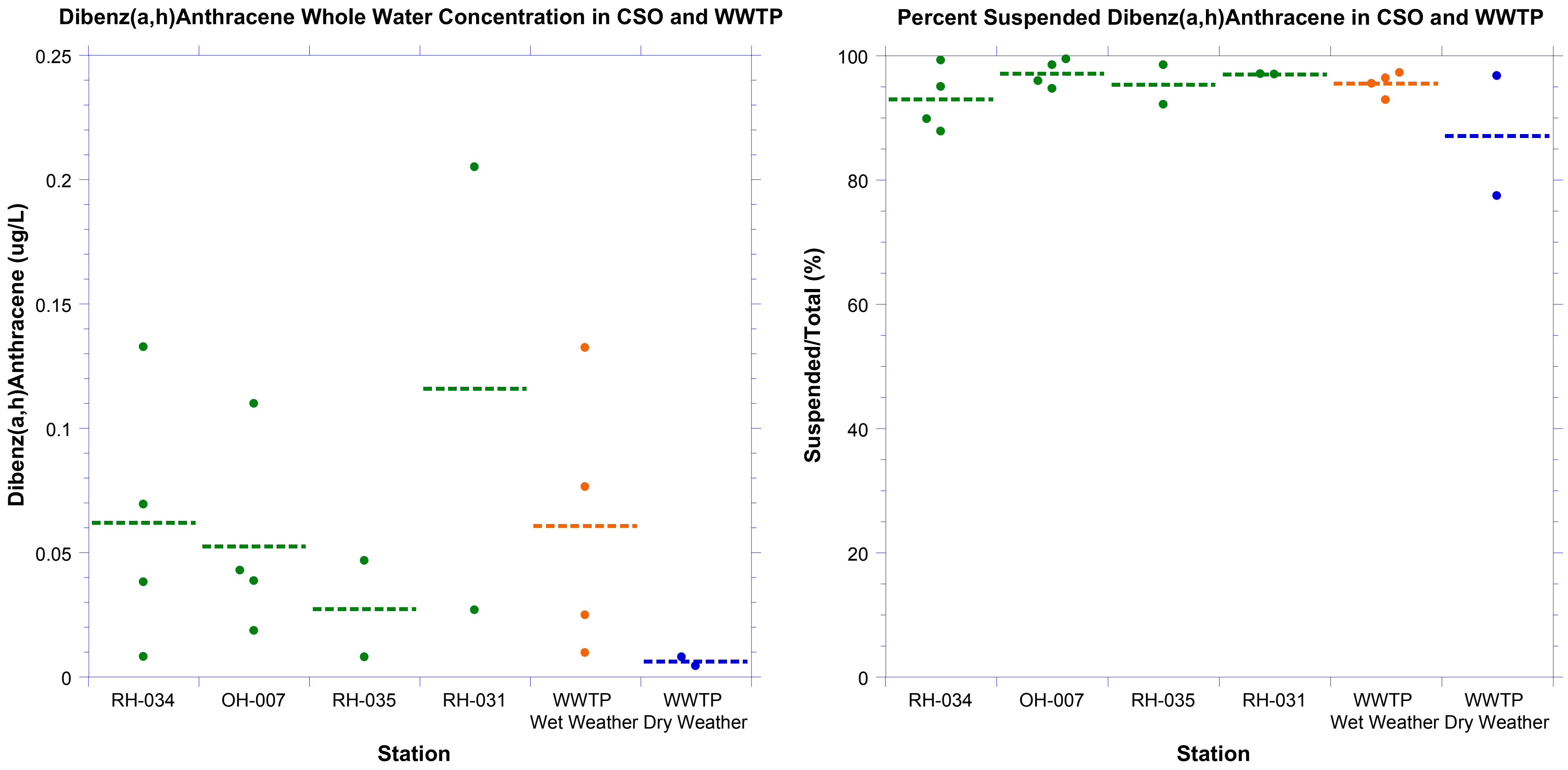


Chrysene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-15b

April 2013



Dibenz(a,h)Anthracene Whole Water Concentration in CSO and WWTP

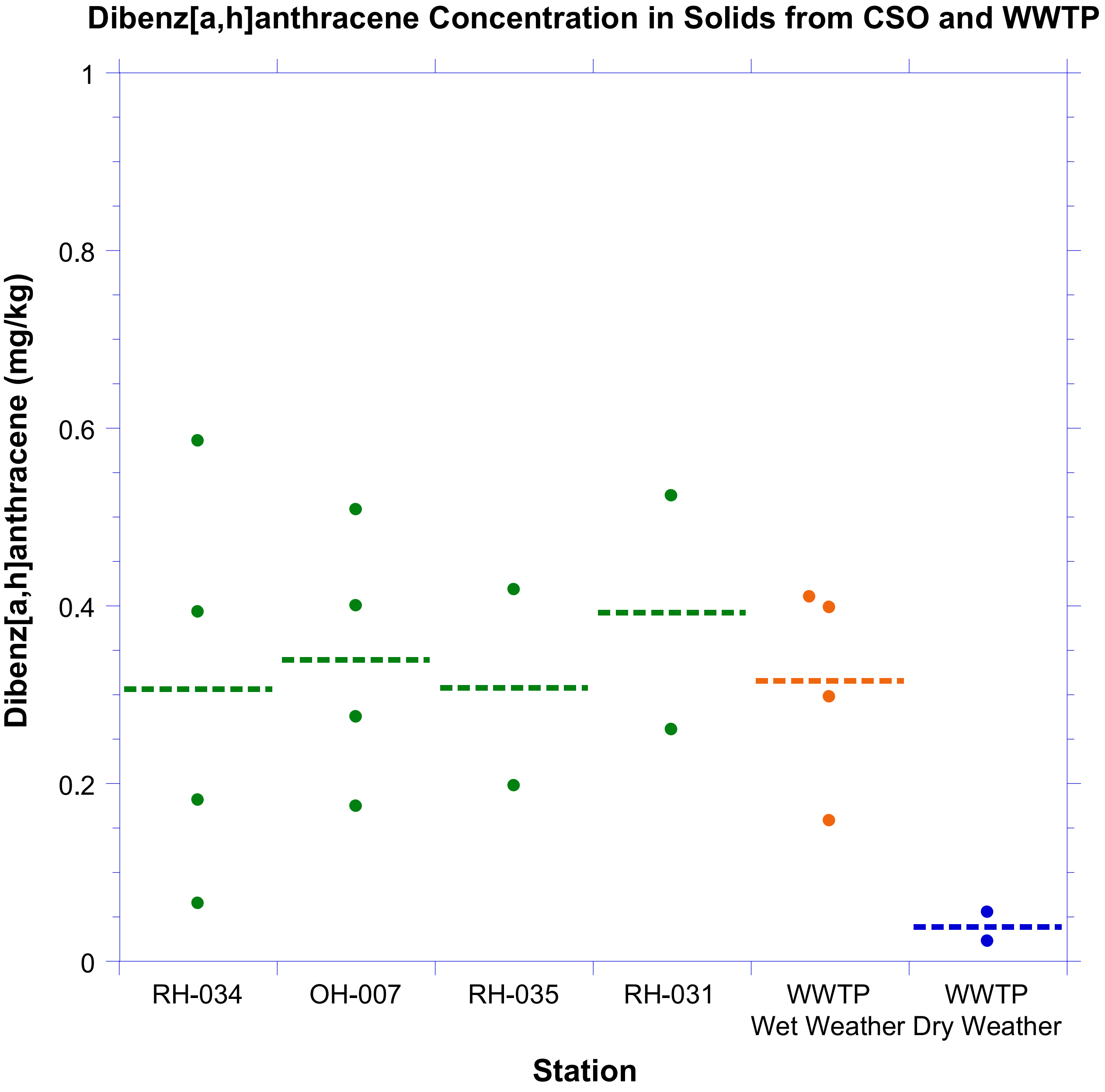
Percent Suspended Dibenz(a,h)Anthracene in CSO and WWTP

Dibenz(a,h)Anthracene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-16a

April 2013

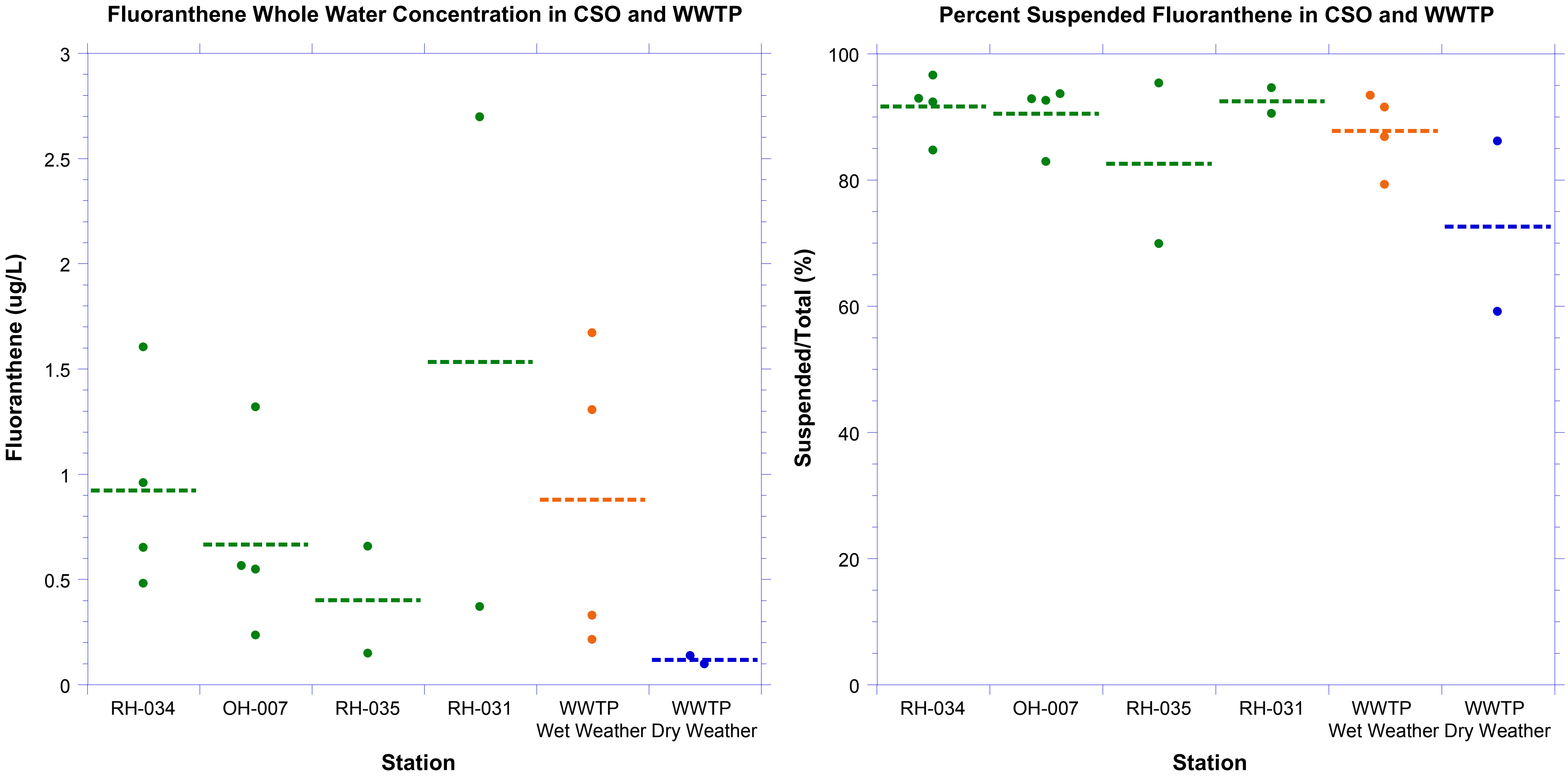


Dibenz(a,h)Anthracene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-16b

April 2013

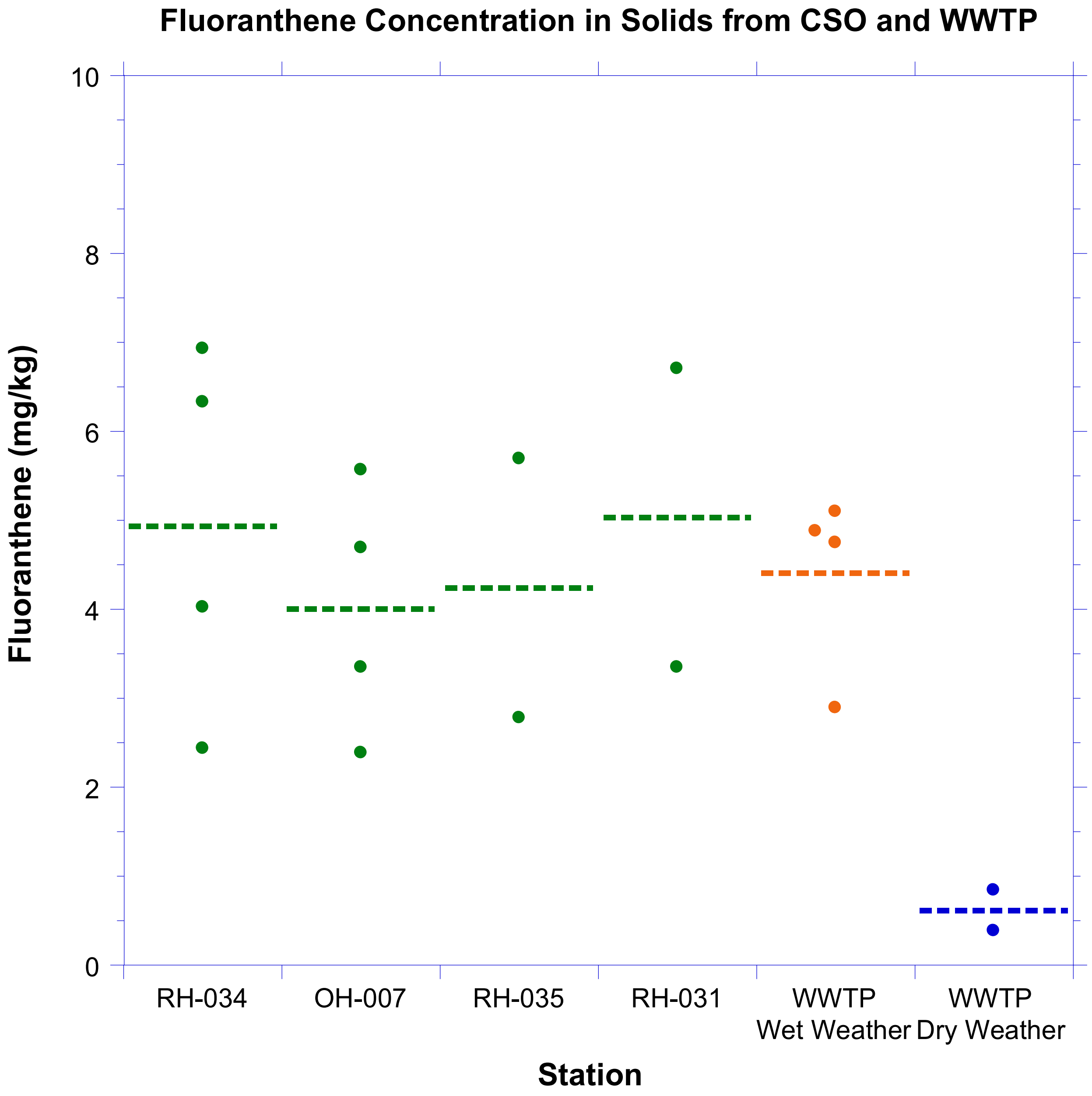


Fluoranthene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-17a

April 2013

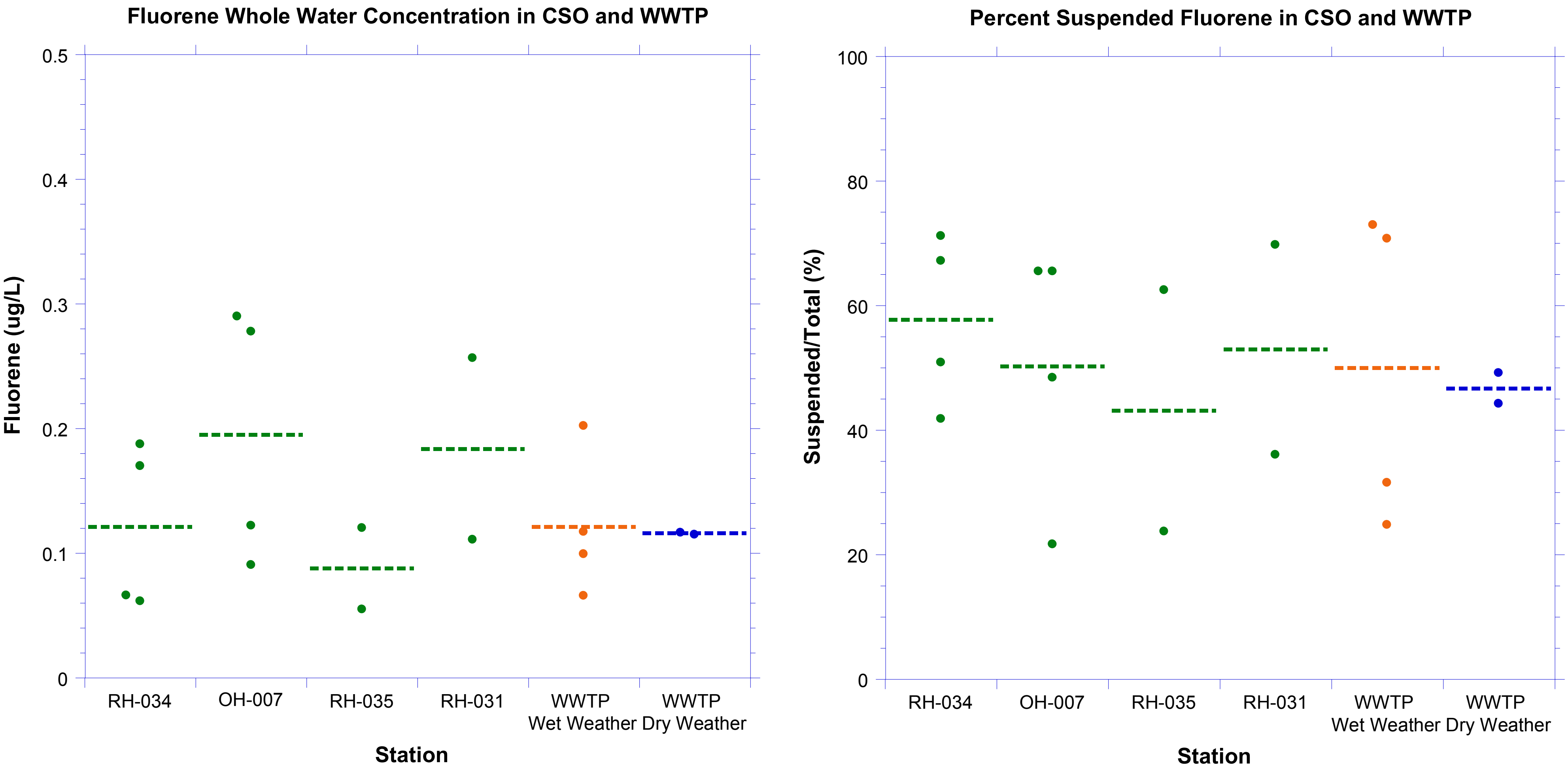


Fluoranthene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-17b

April 2013


Fluorene Whole Water Concentration in CSO and WWTP

Percent Suspended Fluorene in CSO and WWTP

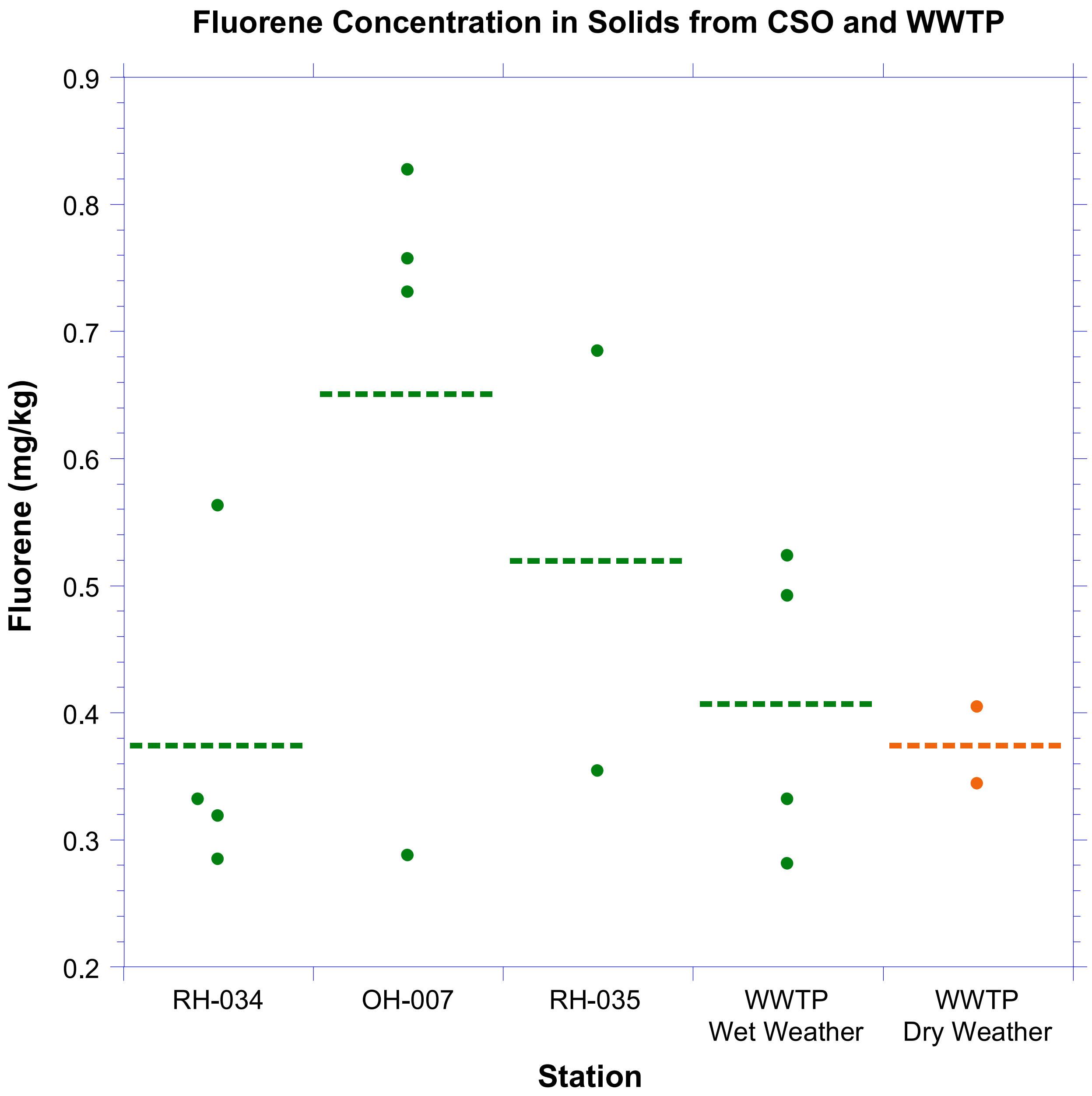
Environmental Protection

Fluorene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-18a

April 2013



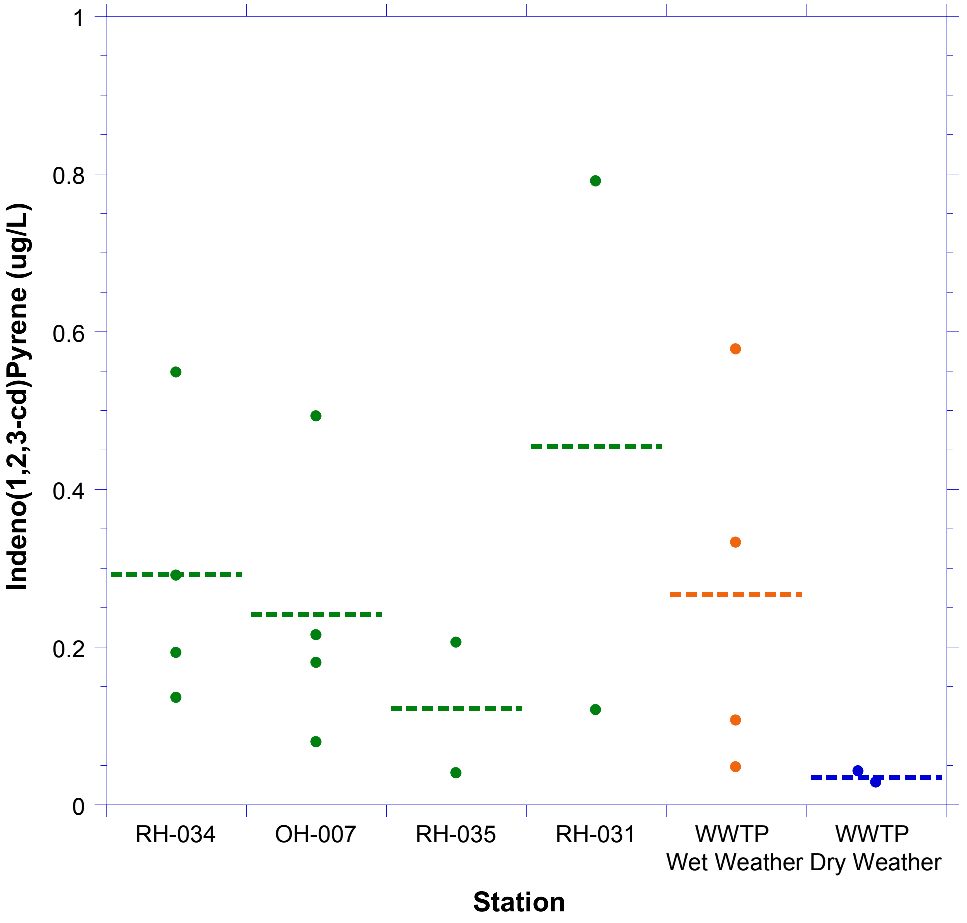
Fluorene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

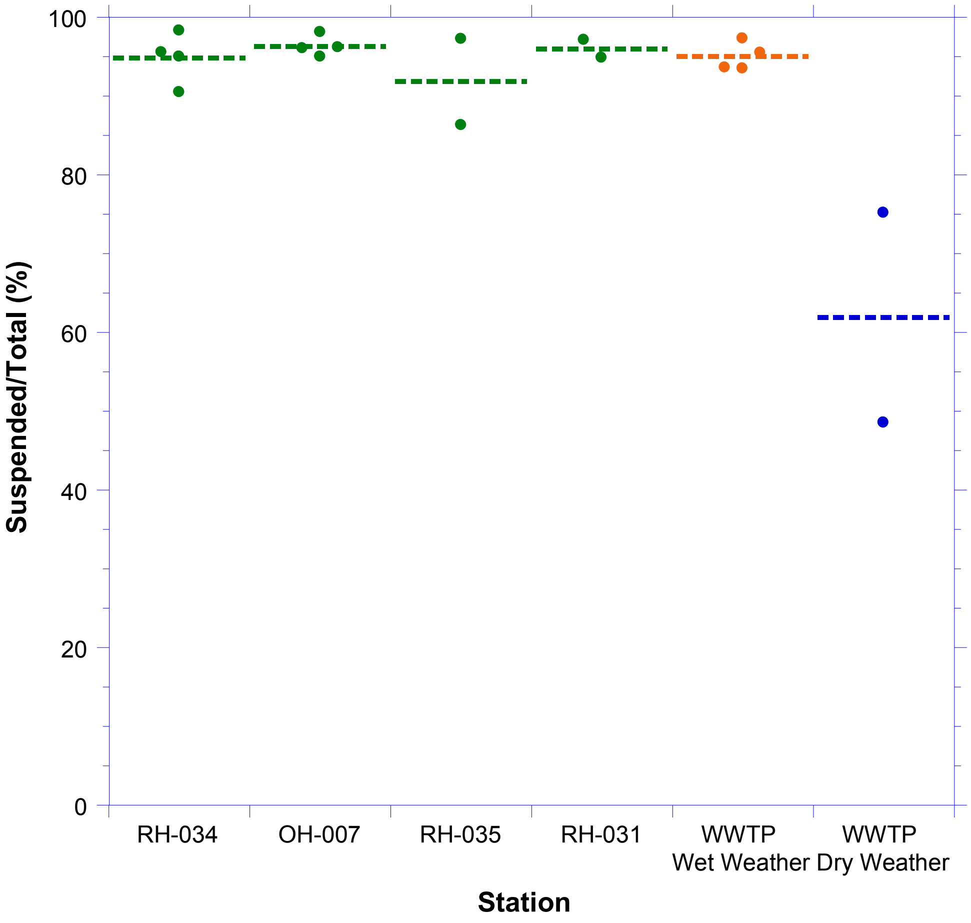
Figure A1-18b

April 2013

Indeno(1,2,3-cd)Pyrene Whole Water Concentration in CSO and WWTP



Percent Suspended Indeno(1,2,3-cd)Pyrene in CSO and WWTP

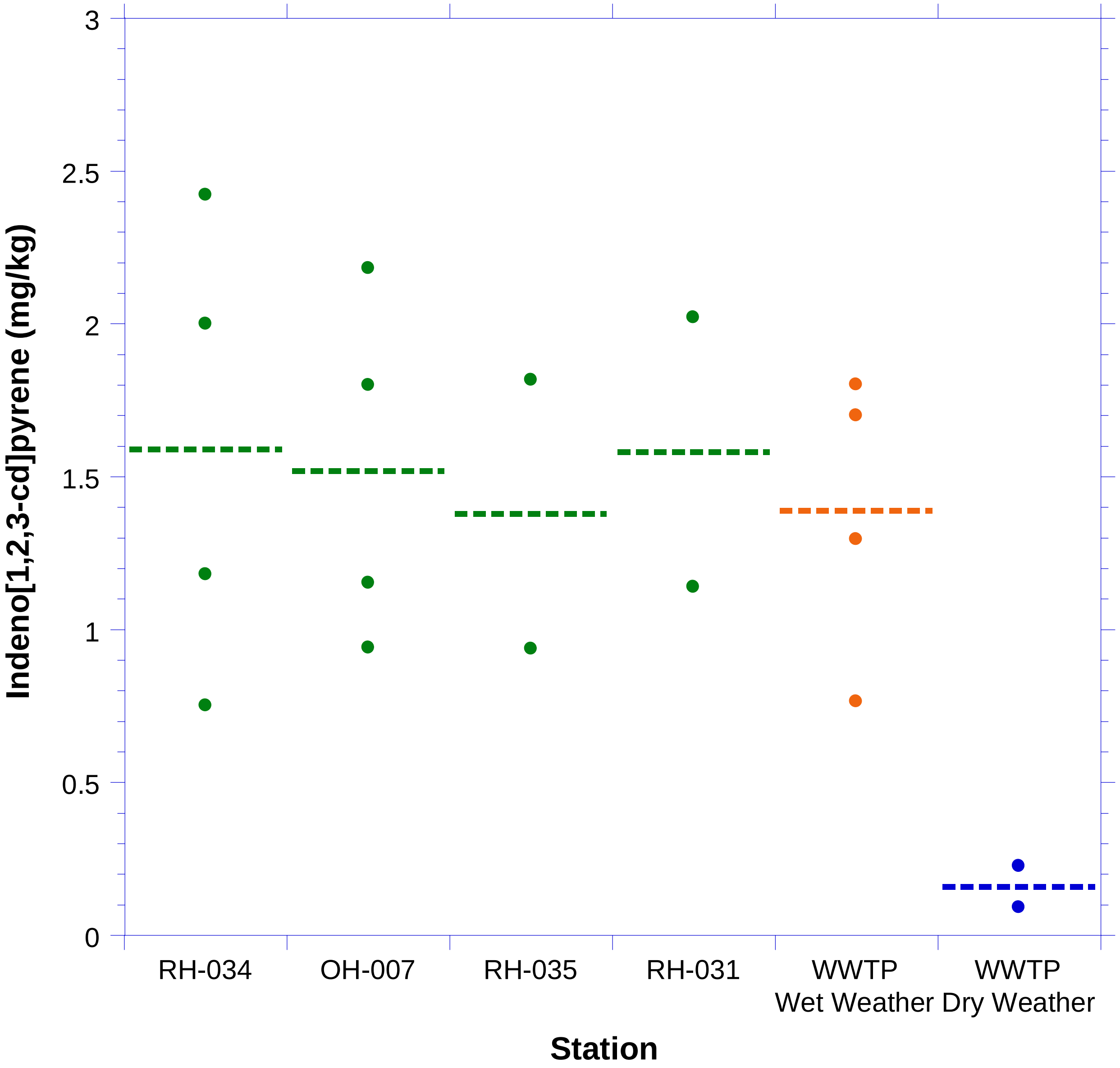


Indeno(1,2,3-cd)Pyrene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-19a

April 2013

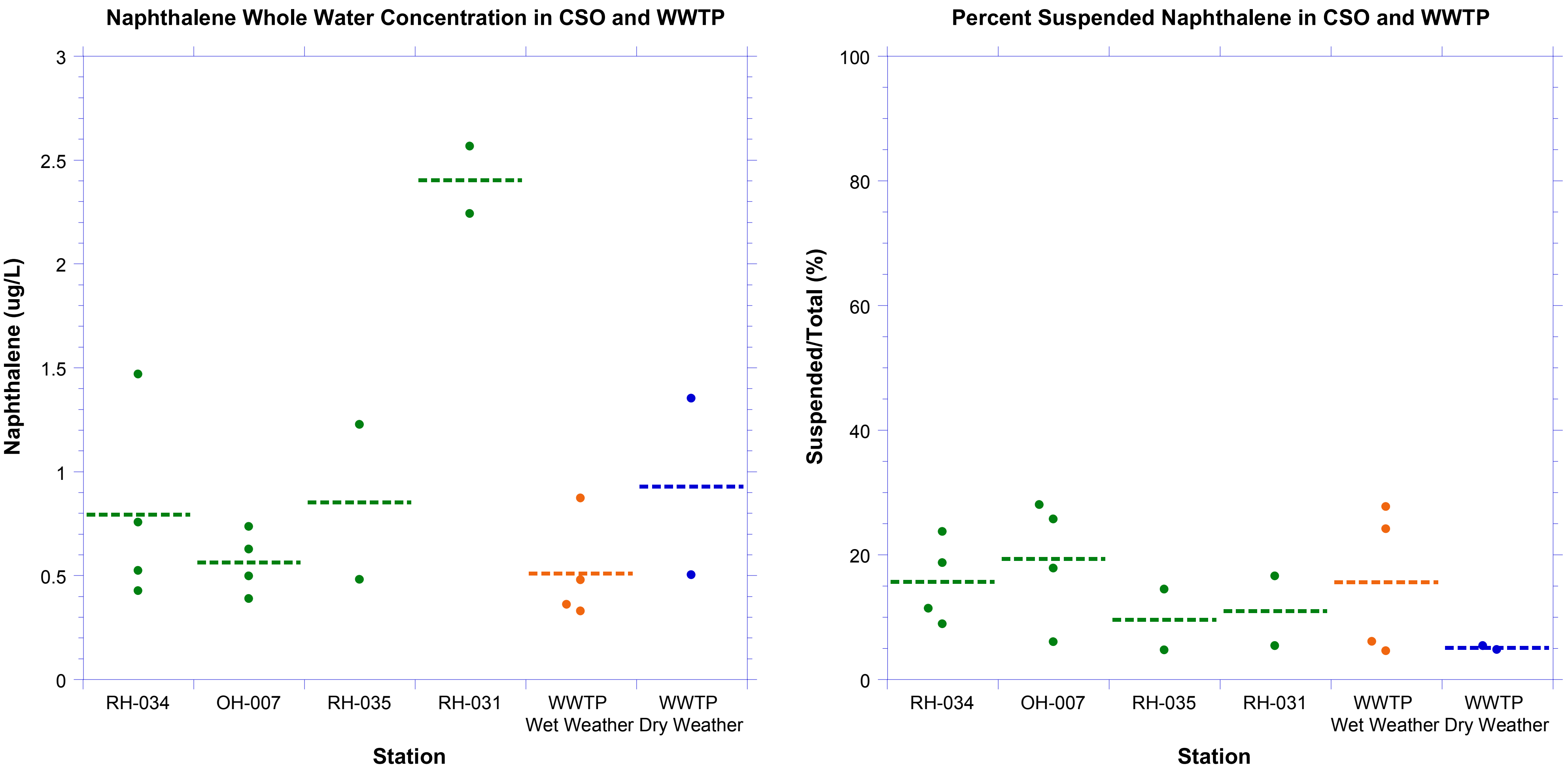


Indeno(1,2,3-cd)Pyrene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-19b

April 2013



Naphthalene Whole Water Concentration in CSO and WWTP

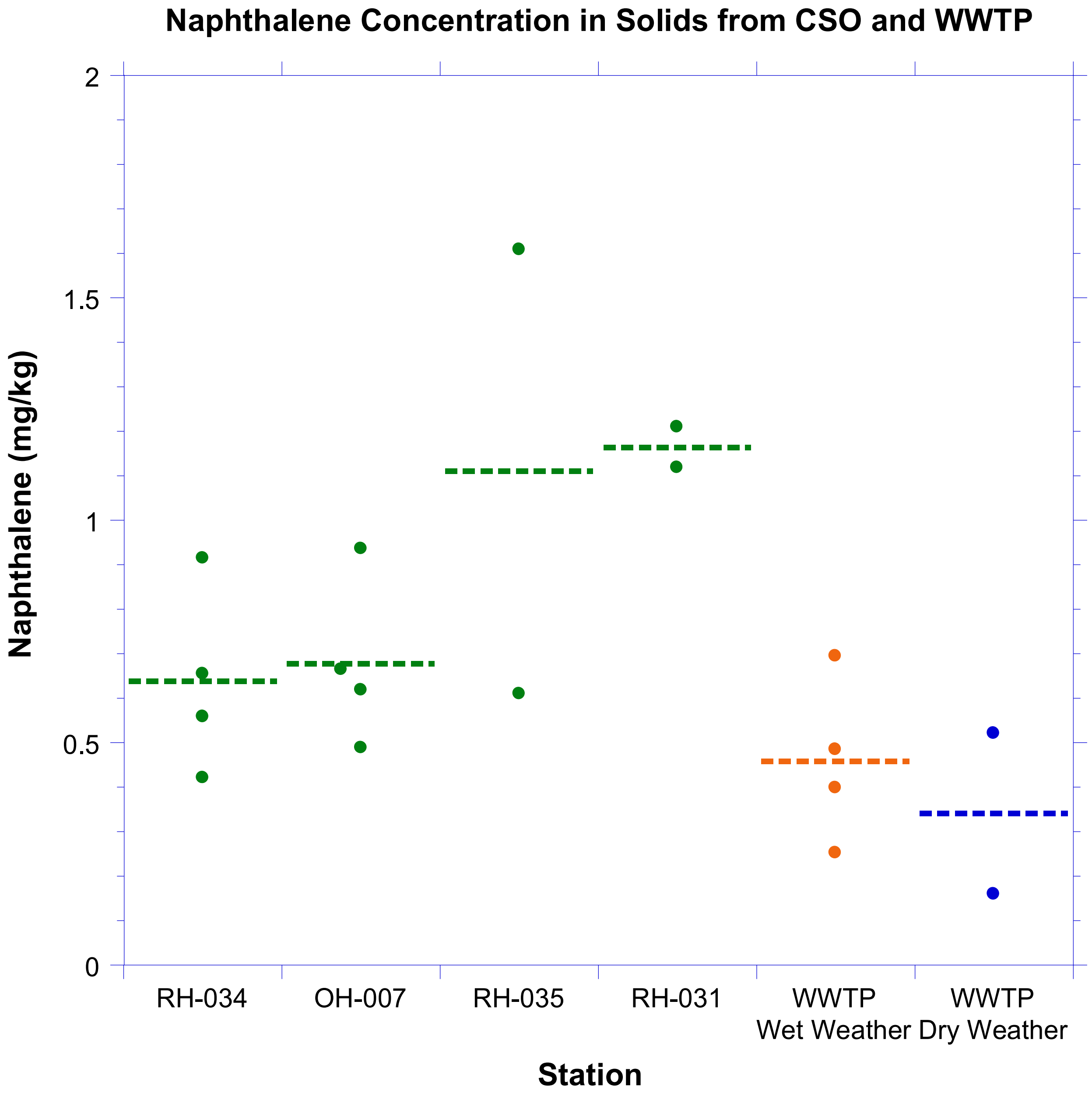
Percent Suspended Naphthalene in CSO and WWTP

Naphthalene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-20a

April 2013

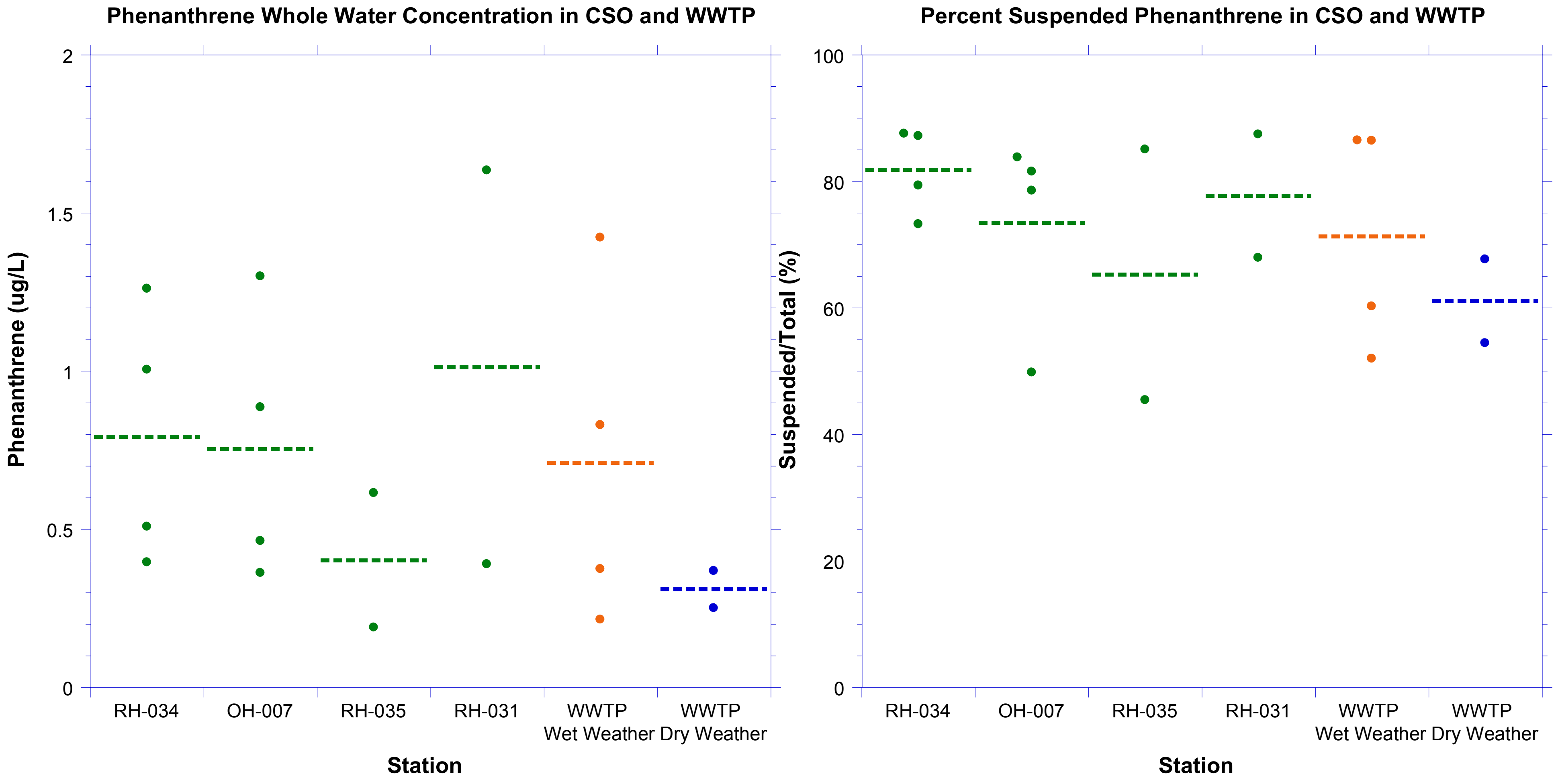


Naphthalene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-20b

April 2013

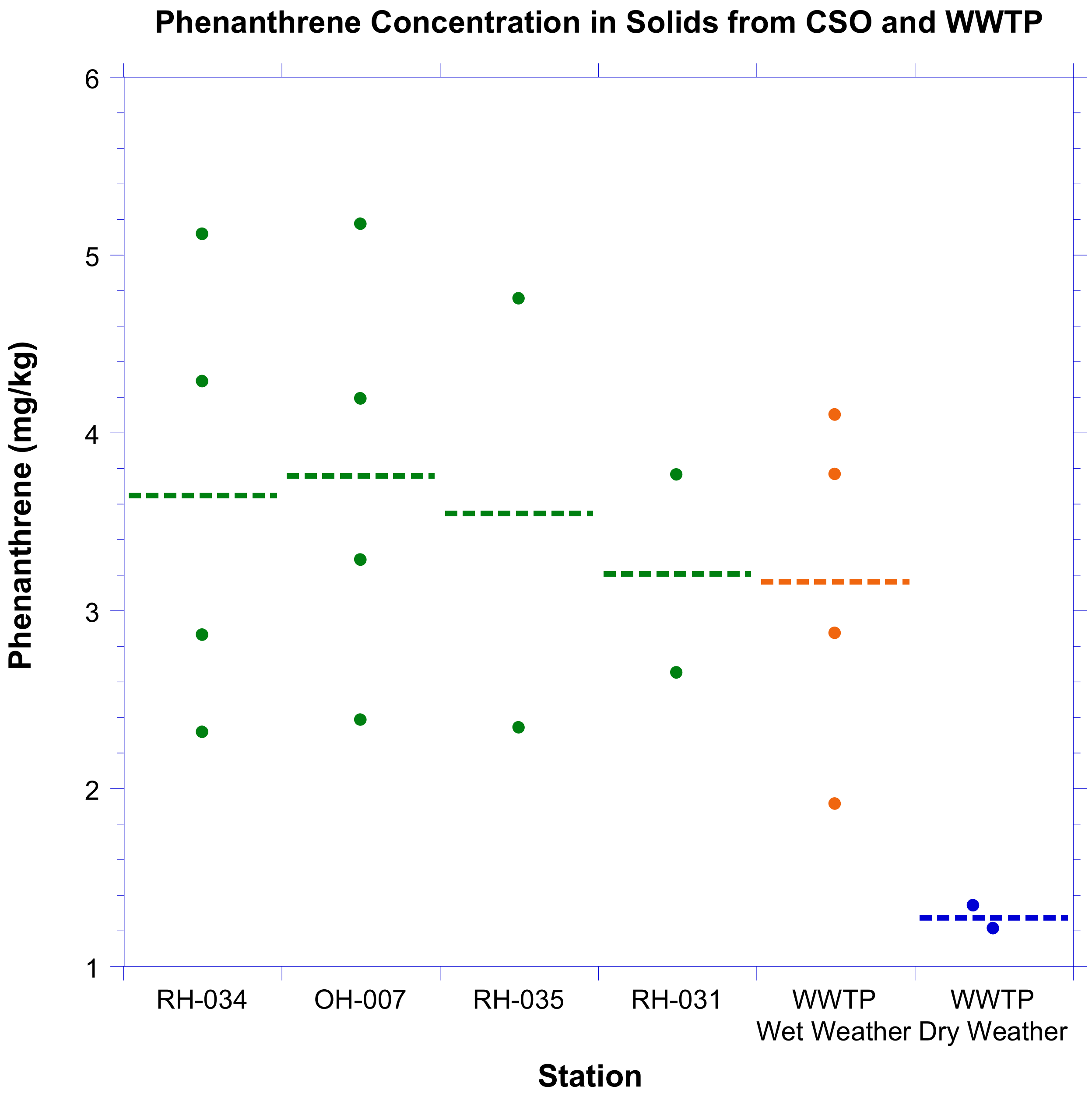


Phenanthrene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-21a

April 2013

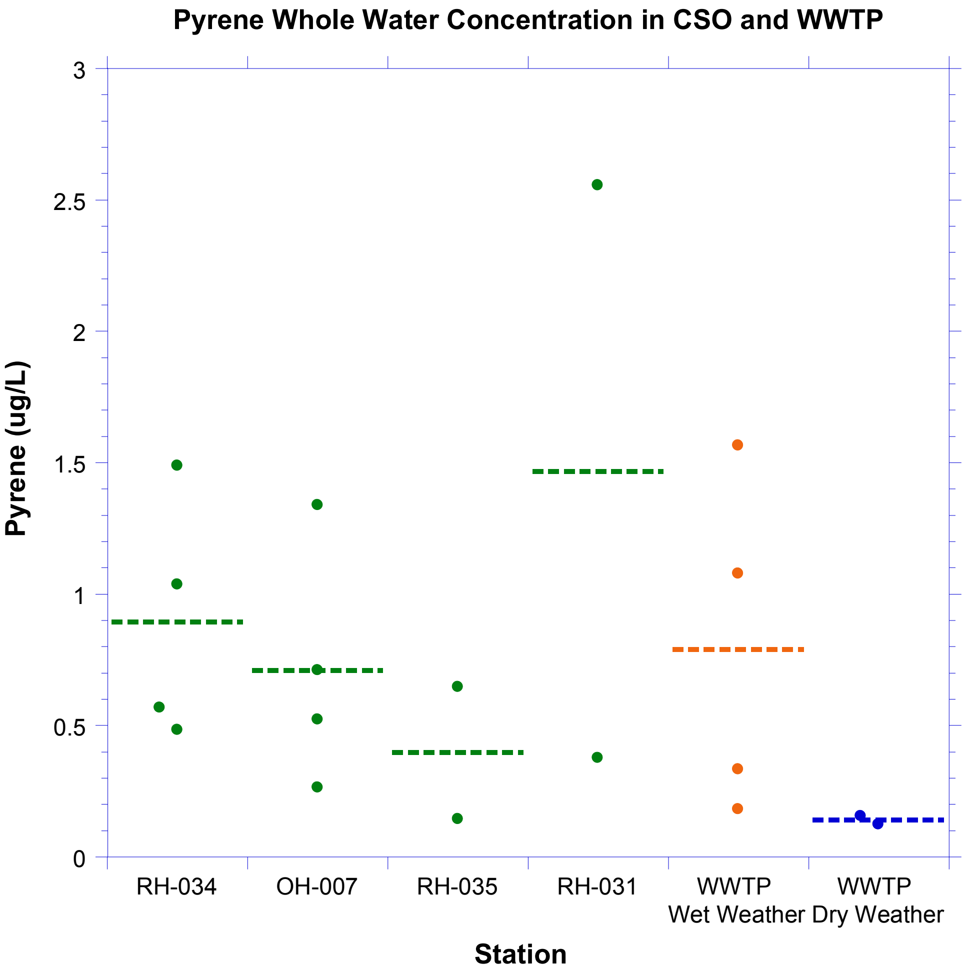


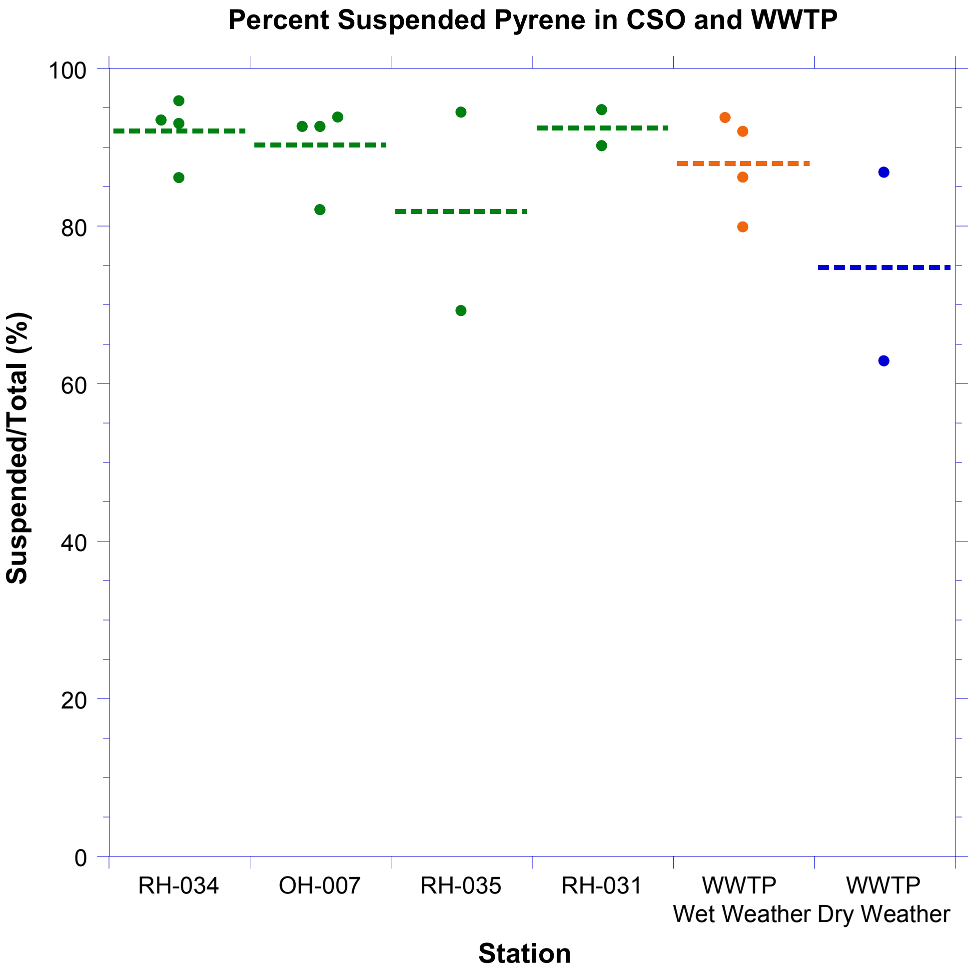
Phenanthrene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-21b

April 2013



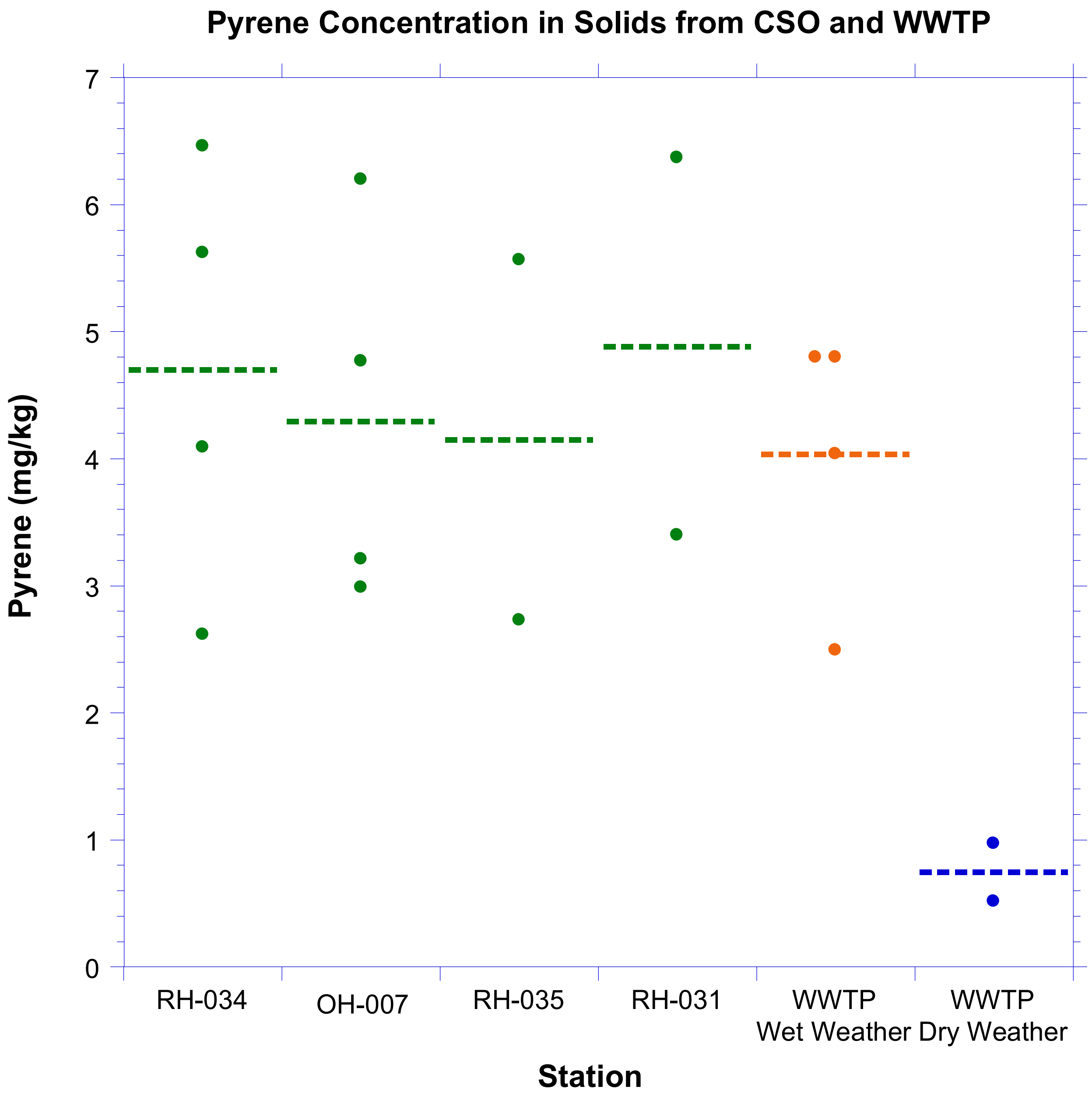


Pyrene Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-22a

April 2013

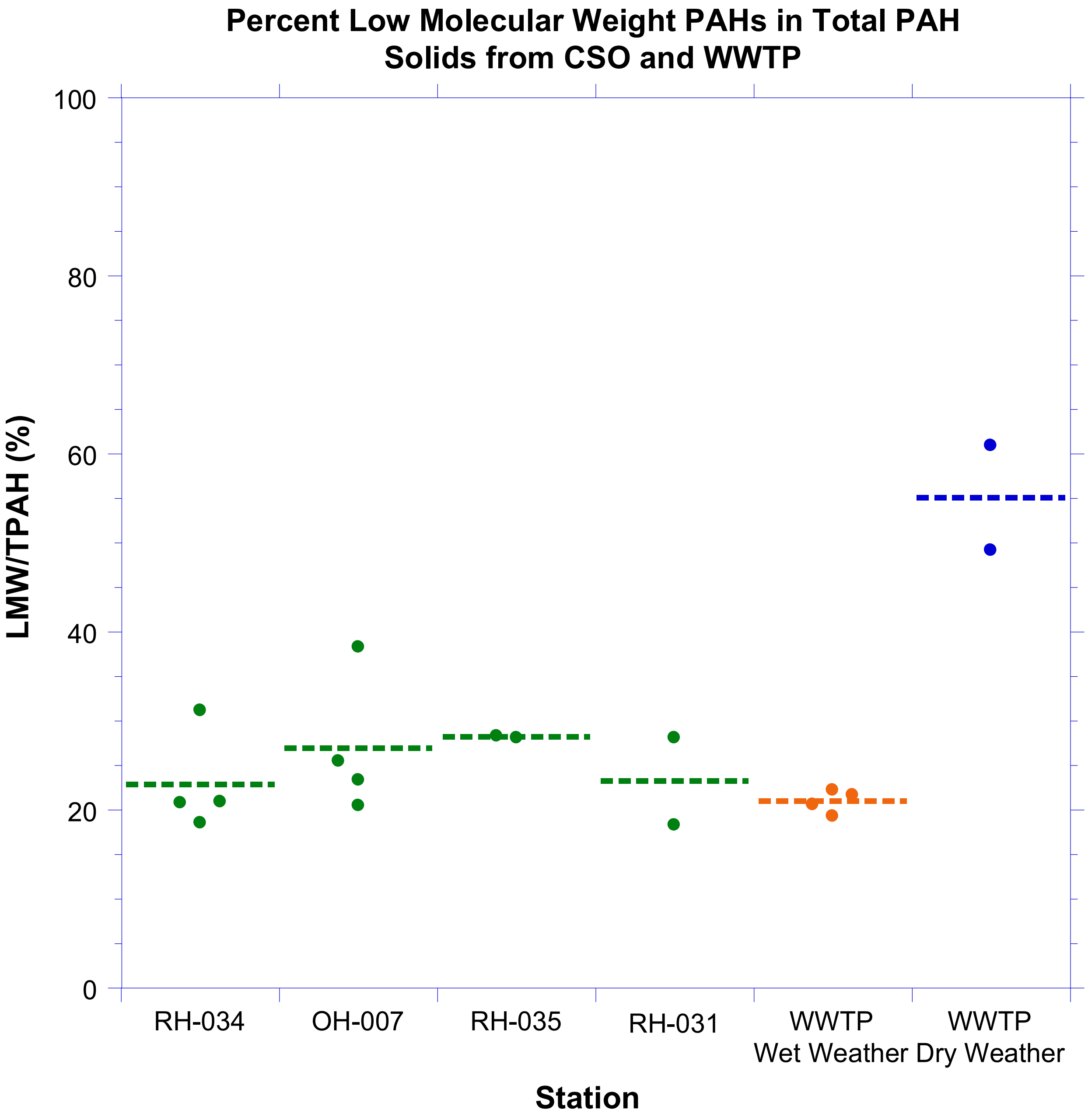


Pyrene Concentration on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-22b

April 2013

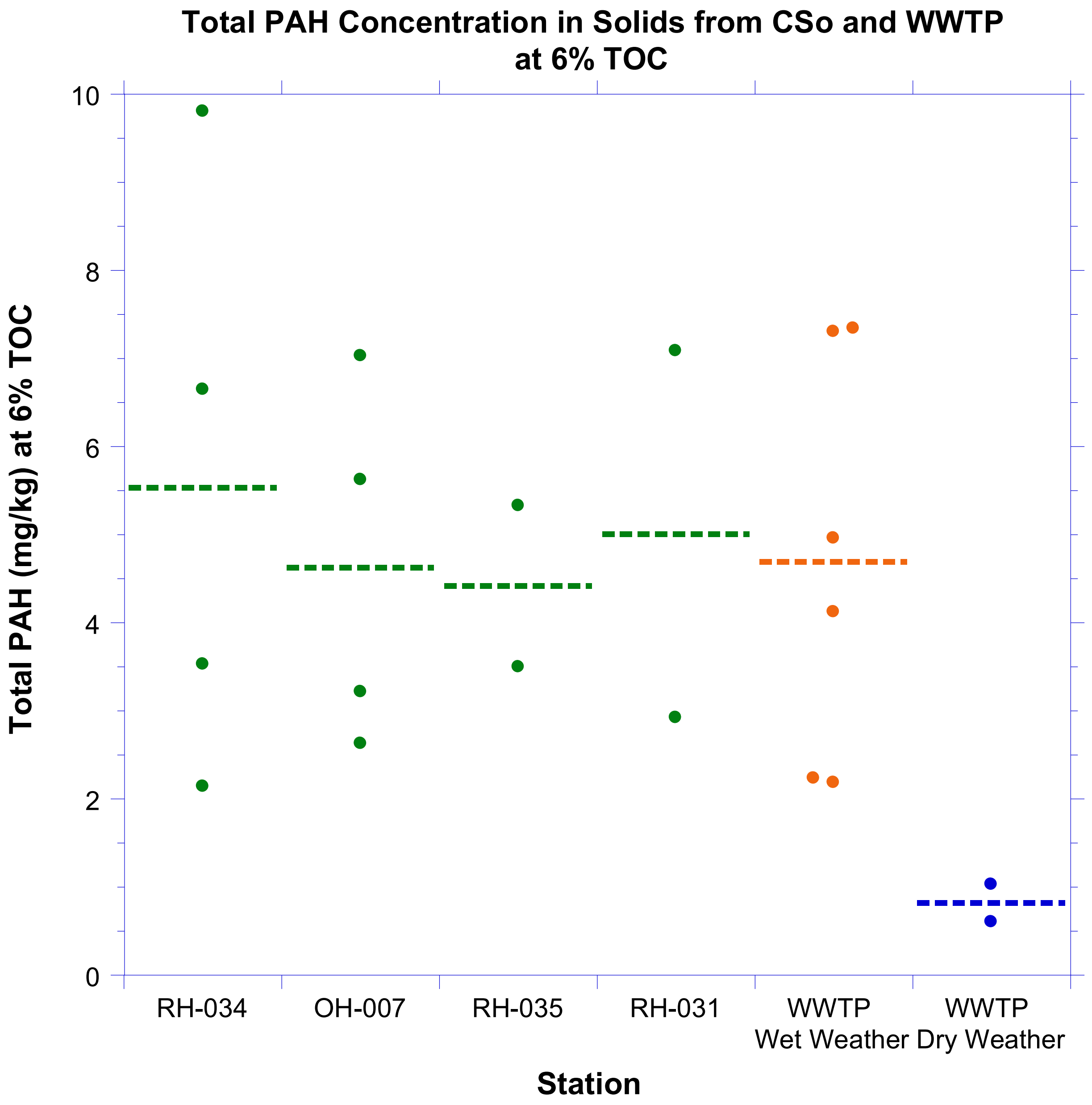


Percent LMW PAHs on Solids from CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-23

April 2013

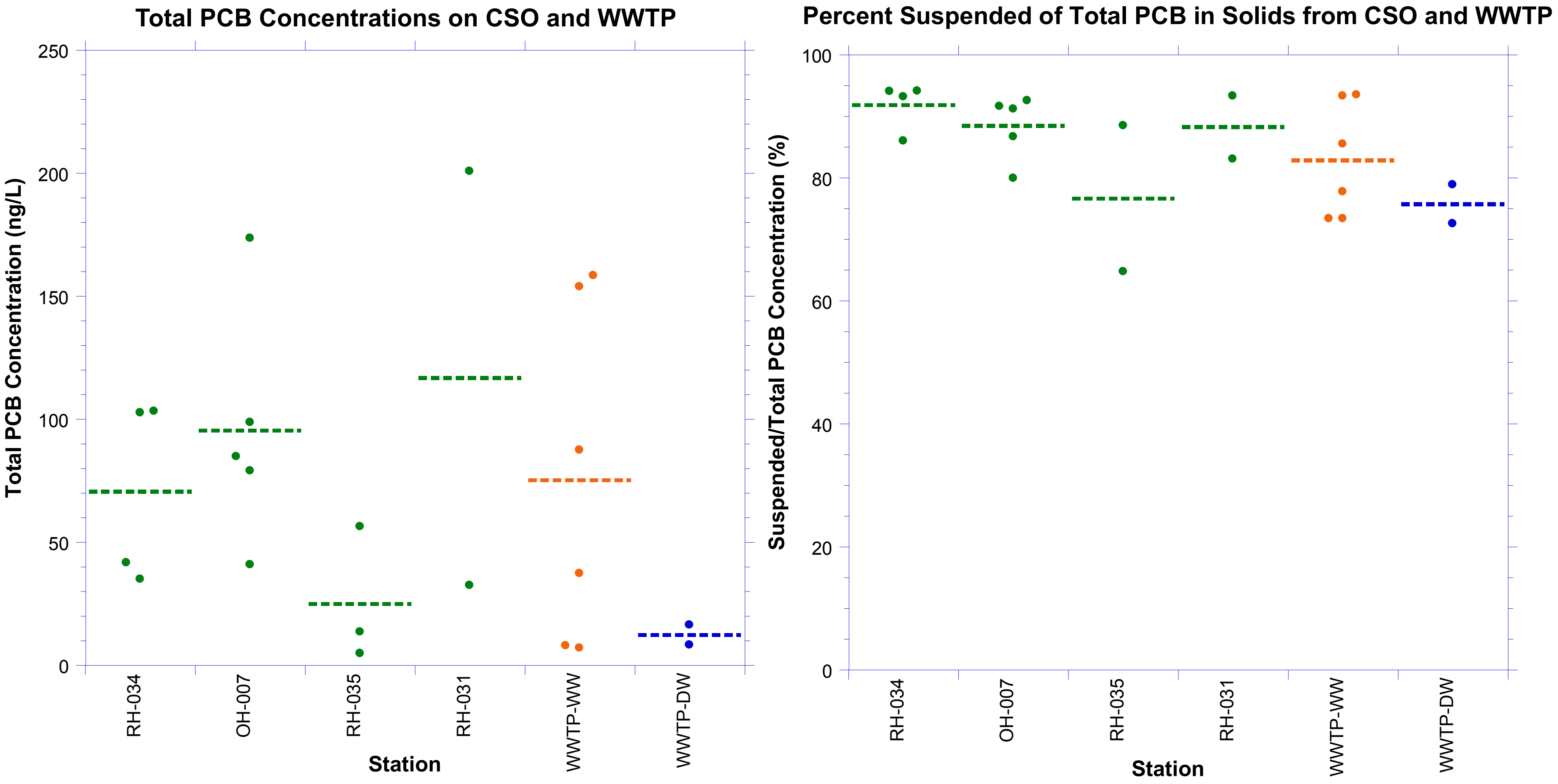


Total PAH Concentration on Solids from CSO and WWTP at 6 % TOC

Gowanus Canal Superfund Site

Figure A1-24

April 2013


Total PCB Concentrations on CSO and WWTP

Percent Suspended of Total PCB in Solids from CSO and WWTP

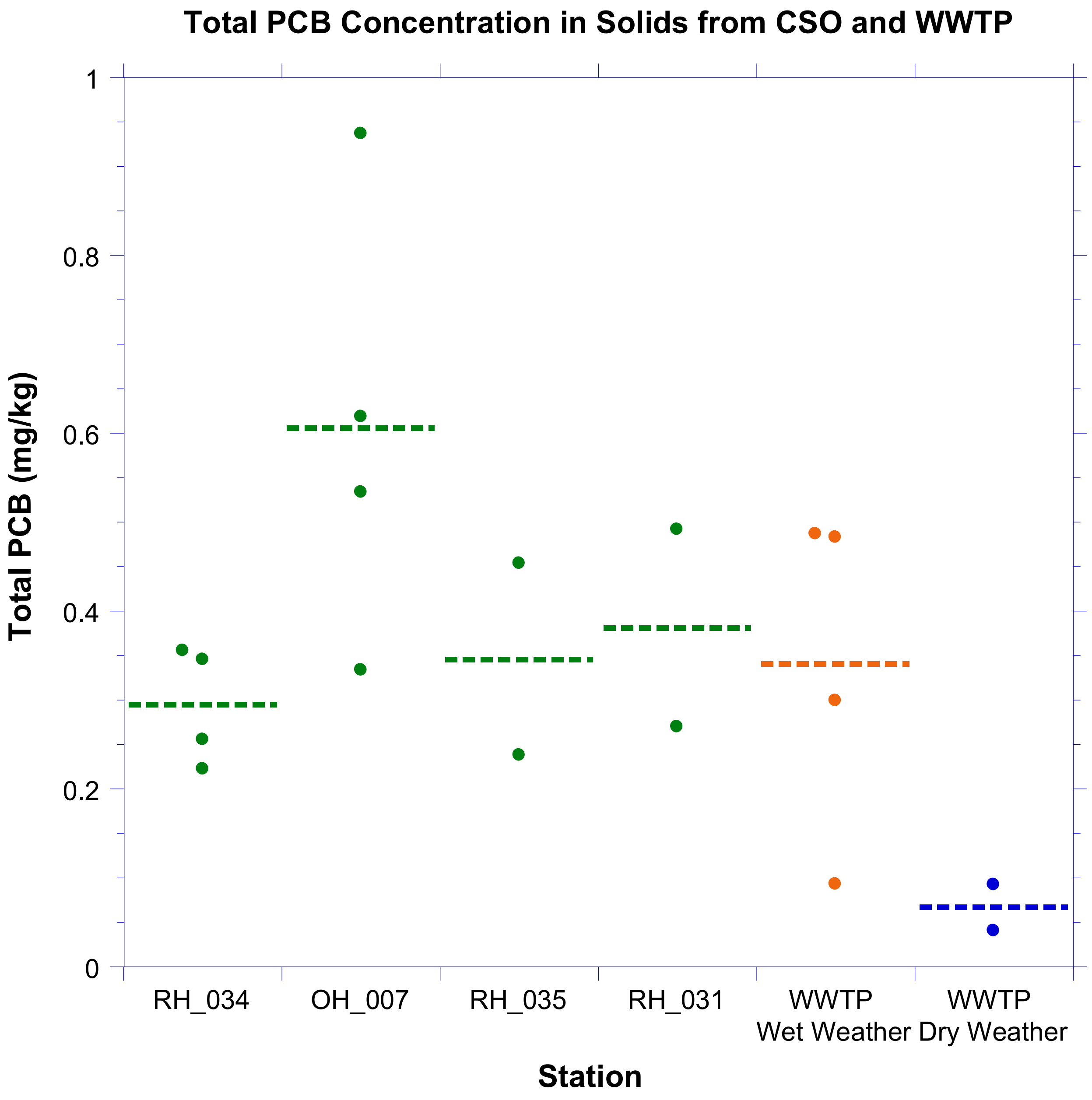
NYC Environmental Protection

Total PCB Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-25a

April 2013

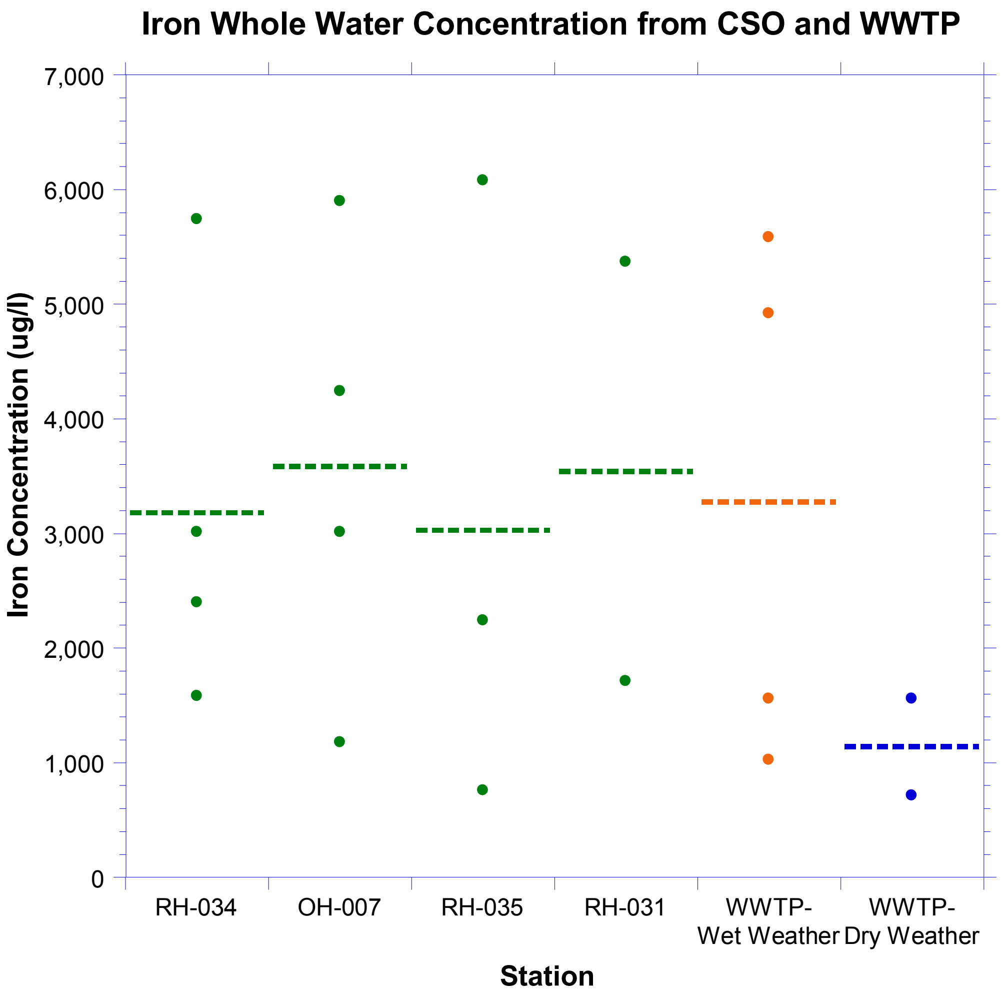


Total PCB Concentration on Solids from CSO and WWTP

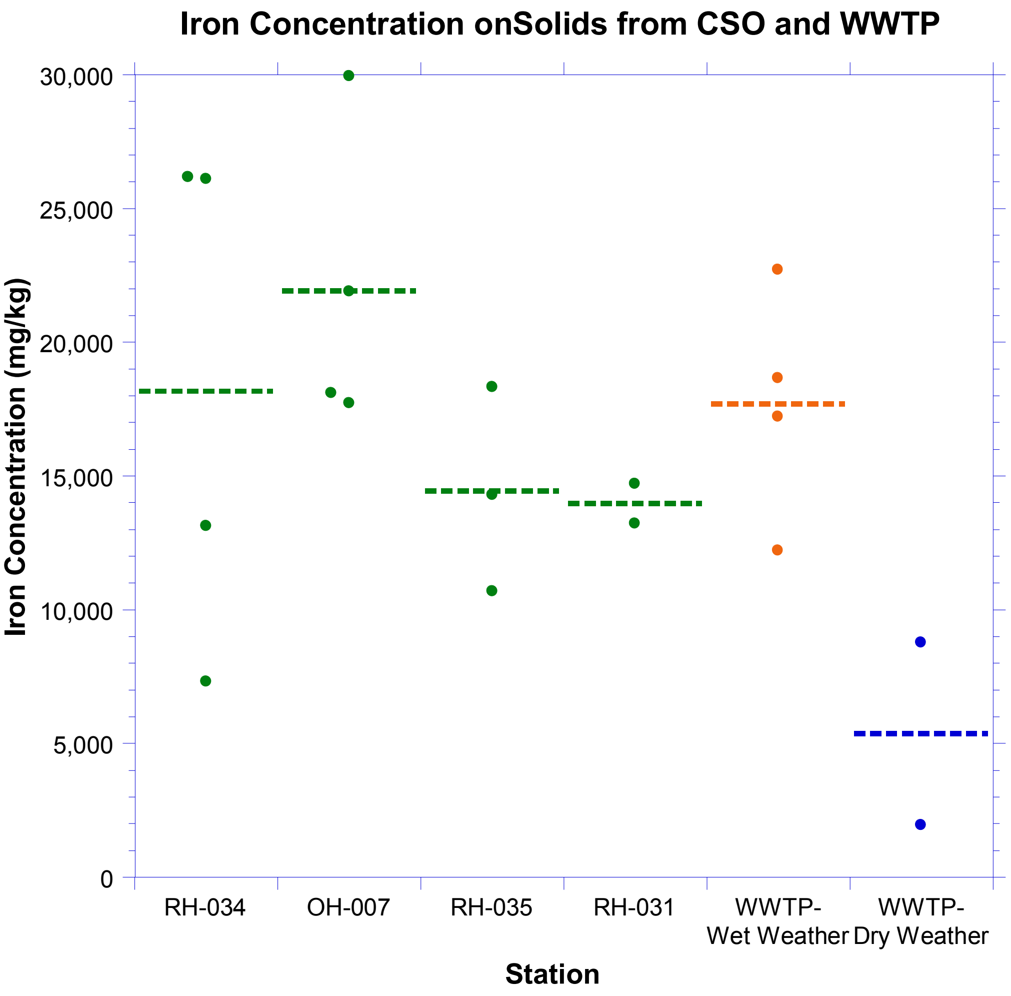
Gowanus Canal Superfund Site

Figure A1-25b

April 2013



Iron Whole Water Concentration from CSO and WWTP



Iron Concentration onSolids from CSO and WWTP

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	3183	3583	3027	3540	3272	1137
SE ug/L	901	996	1585	1830	1157	423

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	18182	21914	14435	13971	17698	5362
SE mg/kg	4746	2838	2204	739	2168	3409

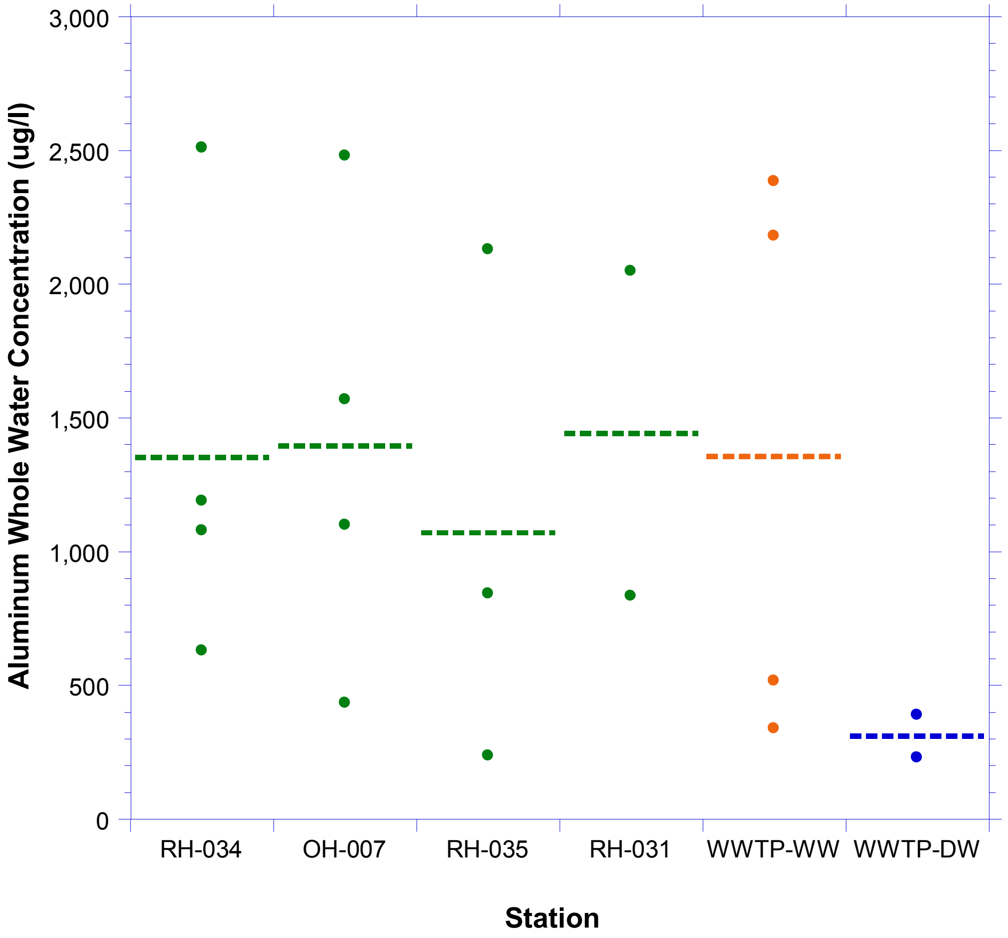
Iron Concentration in CSO and WWTP

Gowanus Canal Superfund Site

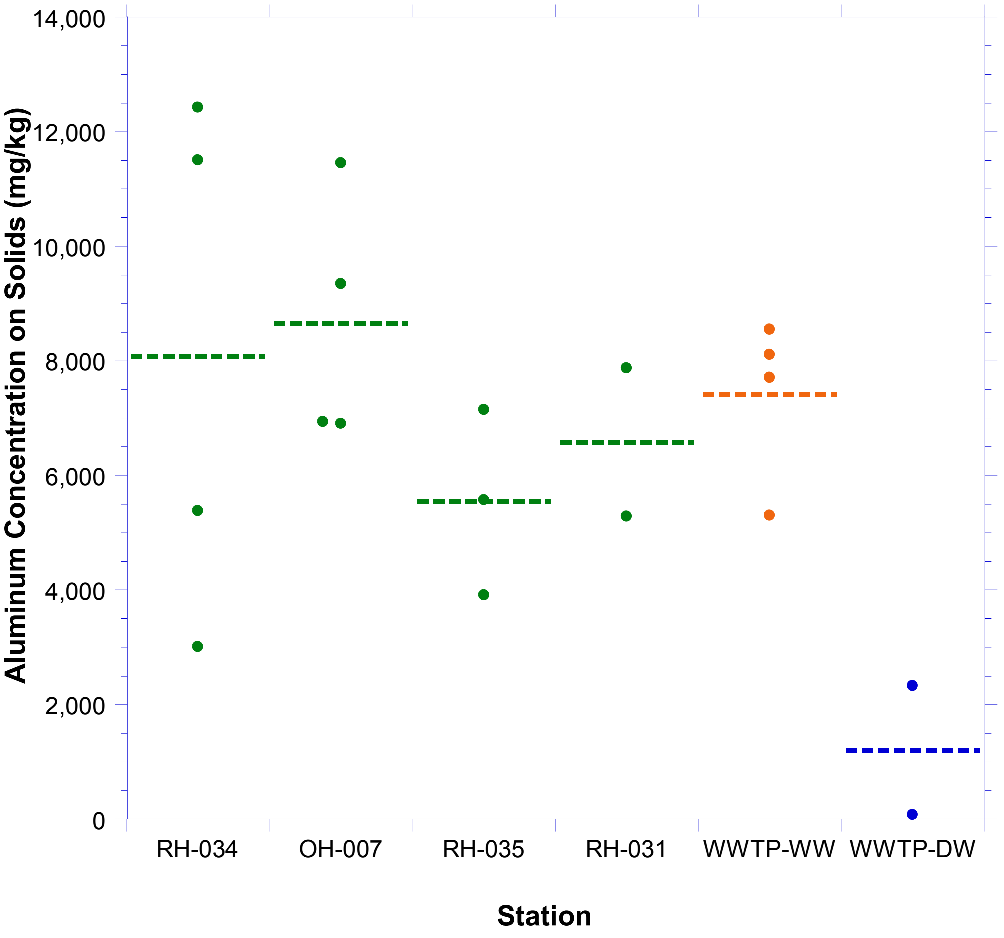
Figure A1-26

April 2013

Aluminum Whole Water Concentration from CSO and WWTP



Aluminum Concentration onSolids from CSO and WWTP



	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	1353	1396	1071	1443	1356	311
SE ug/L	404	430	558	608	538	80

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	8074	8654	5538	6570	7412	1198
SE mg/kg	2301	1093	934	1295	727	1125

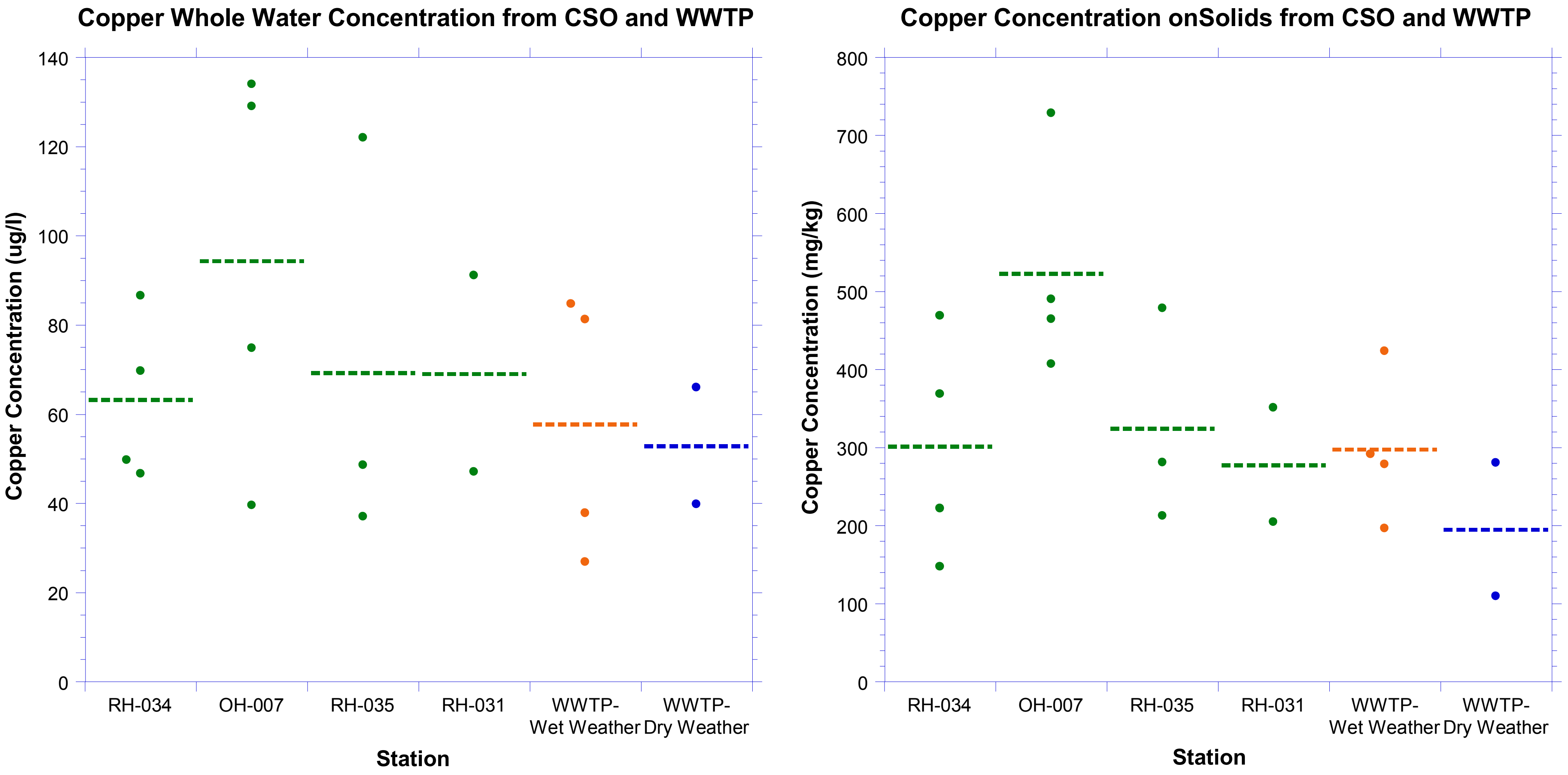
Environmental Protection

Aluminum Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-27

April 2013



	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	63	94	69	69	58	53
SE ug/L	9	23	27	22	15	13

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	302	523	324	278	298	195
SE mg/kg	72	71	80	73	47	86

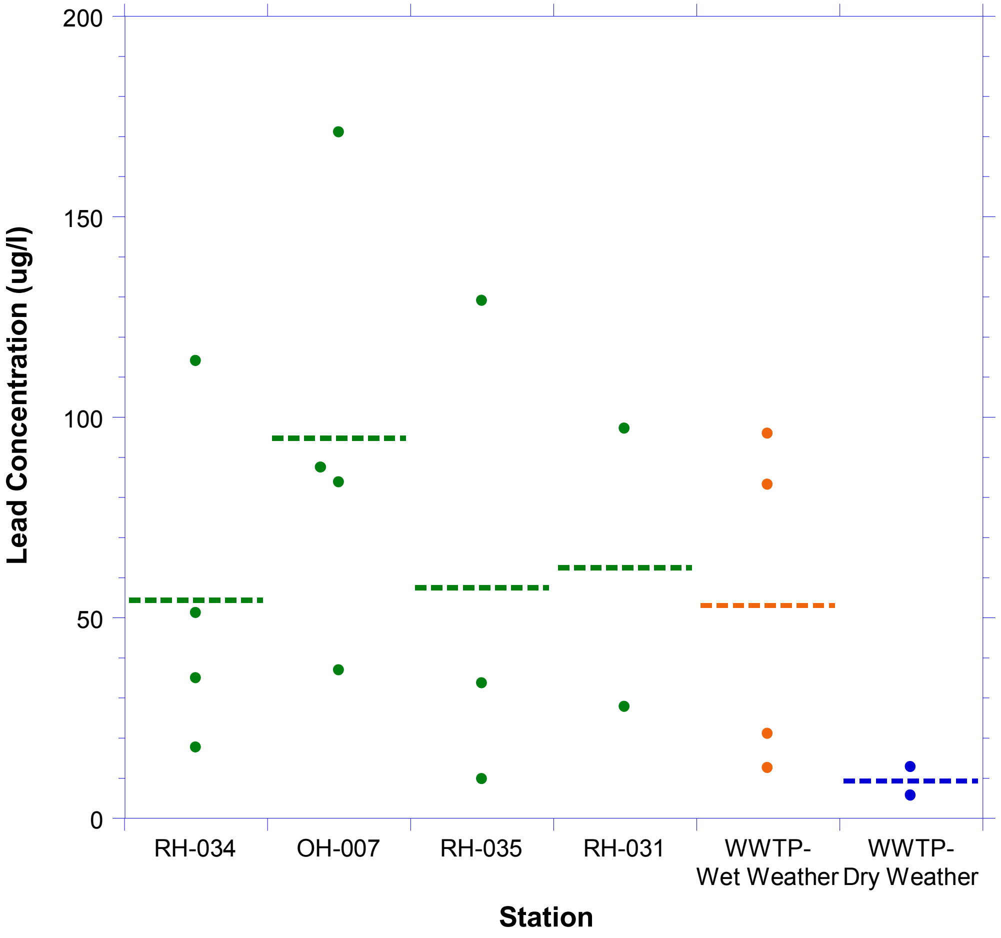
Environmental Protection

Copper Concentration in CSO and WWTP

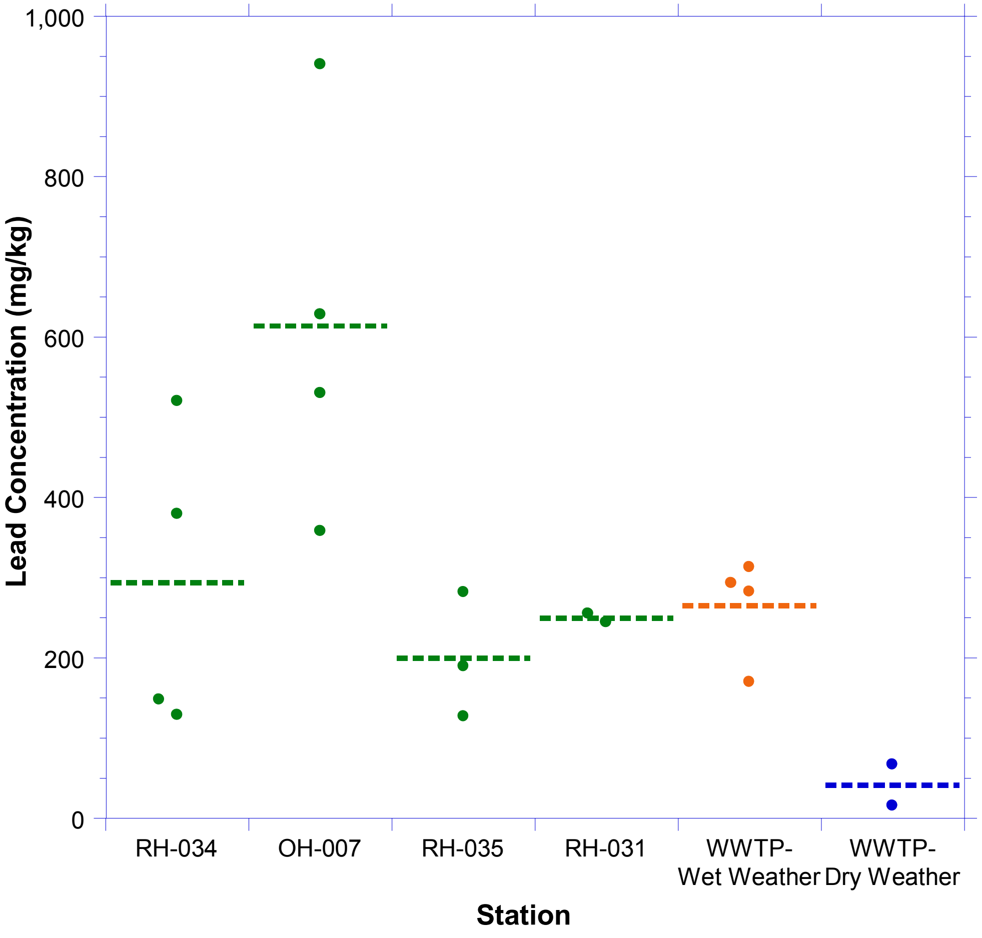
Gowanus Canal Superfund Site

Figure A1-28

April 2013



Lead Whole Water Concentration from CSO and WWTP



Lead Concentration onSolids from CSO and WWTP

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	54	95	57	63	53	9
SE ug/L	21	28	36	35	21	4

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	294	614	199	250	265	42
SE mg/kg	94	122	45	5	32	26

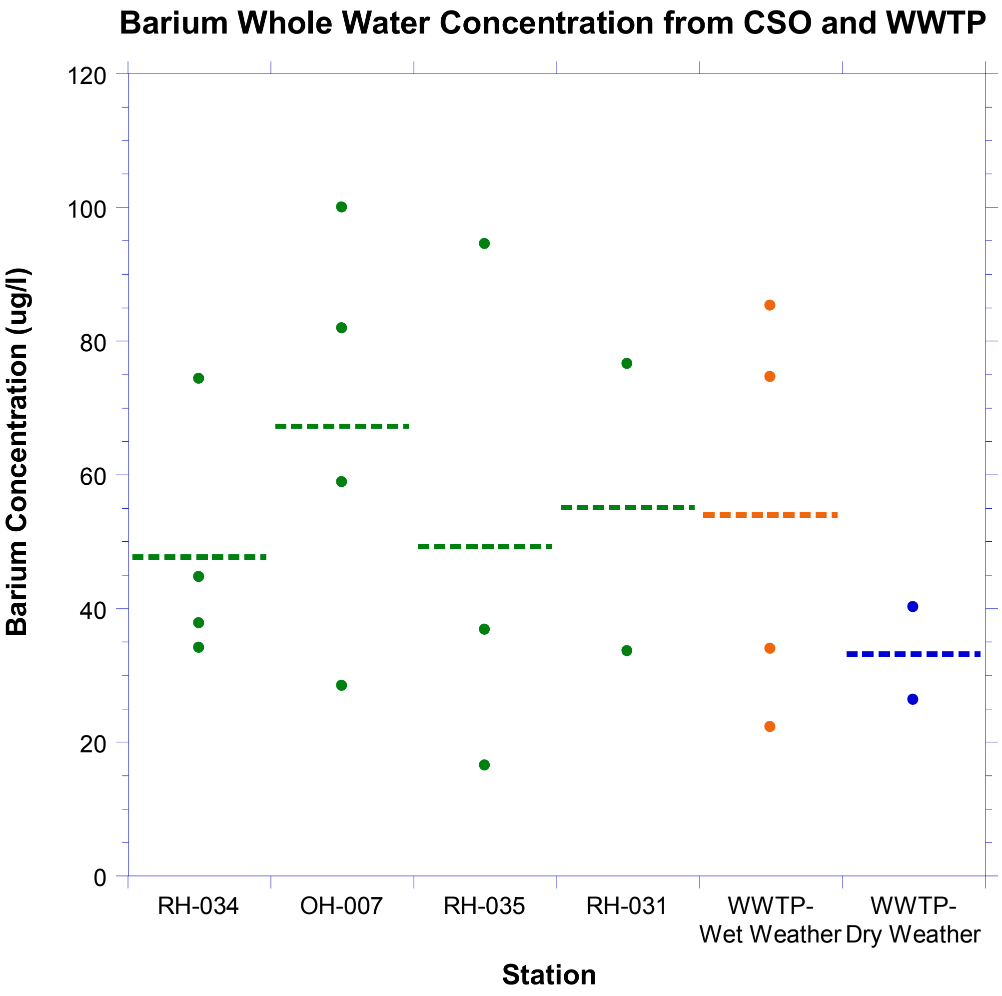
Environmental Protection

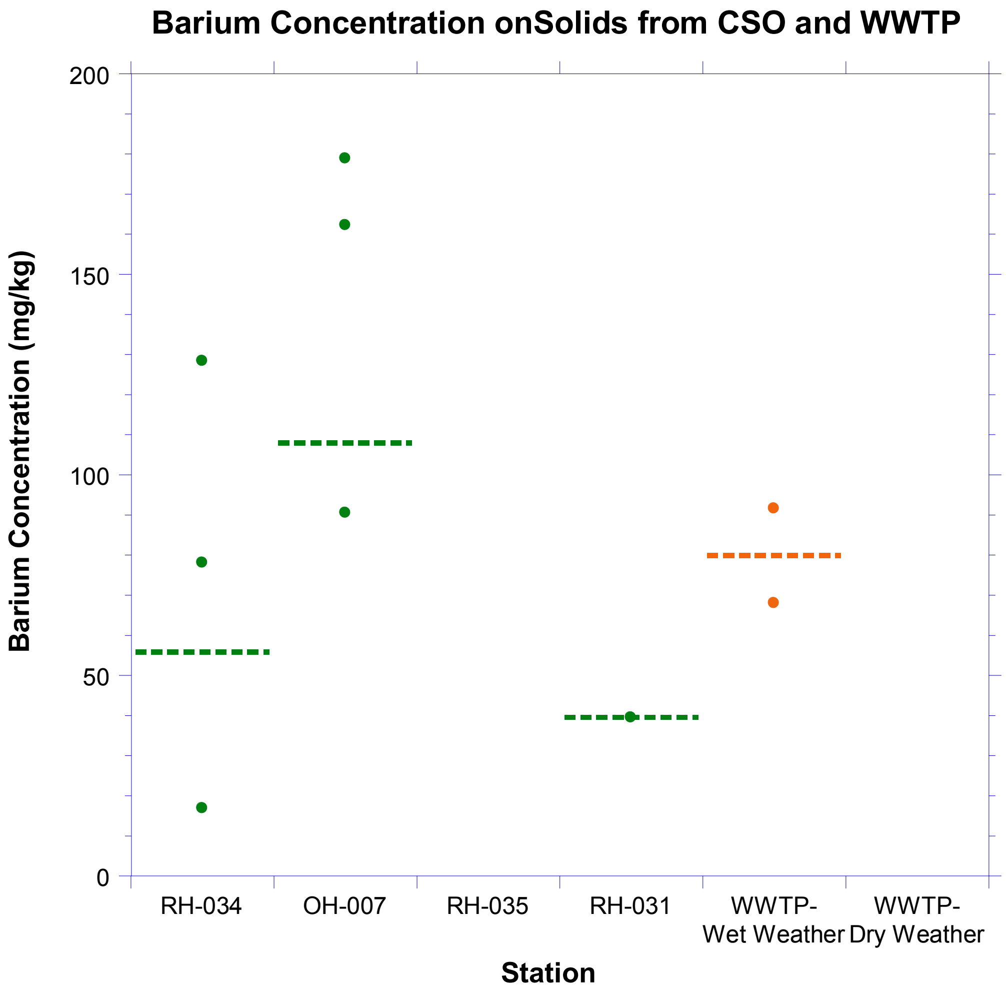
Lead Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-29

April 2013


Barium Whole Water Concentration from CSO and WWTP


Barium Concentration onSolids from CSO and WWTP

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	48	67	49	55	54	33
SE ug/L	9	15	23	22	15	7

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	74.5	143.9		39.5	79.8	
SE mg/kg	32.2	27.1			11.8	

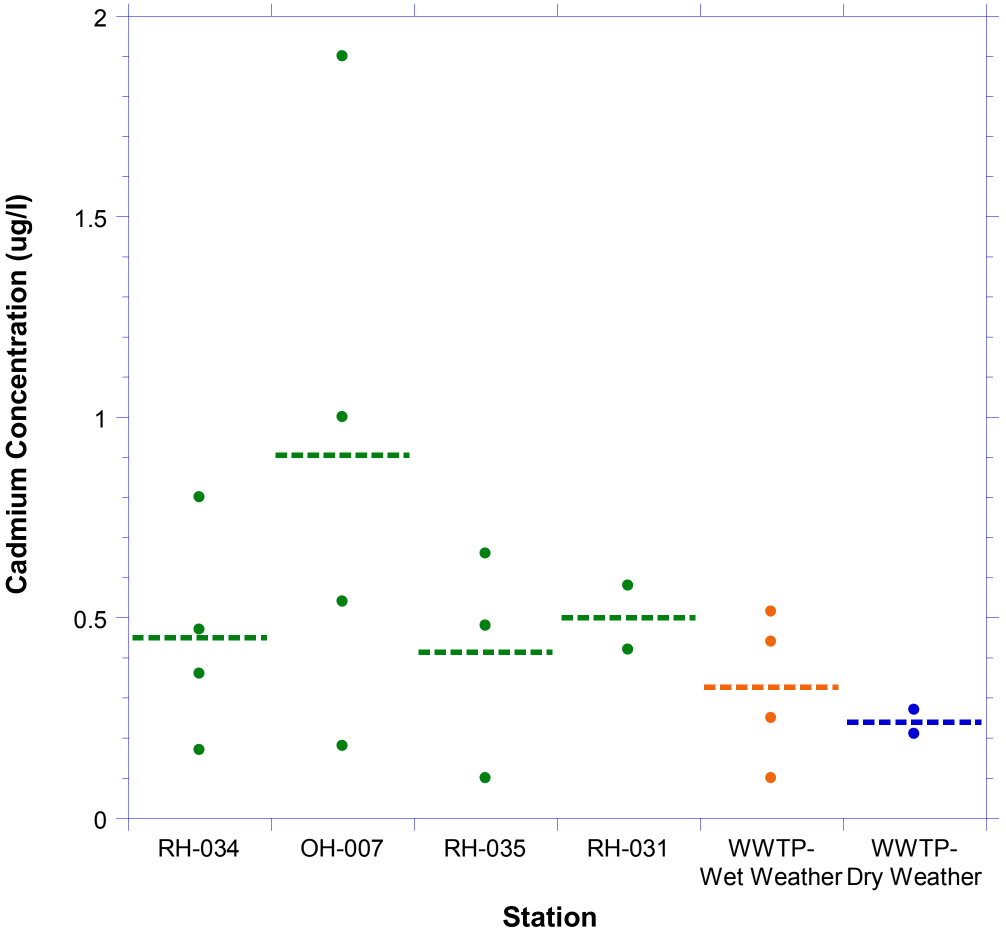
Barium Concentration in CSO and WWTP

Gowanus Canal Superfund Site

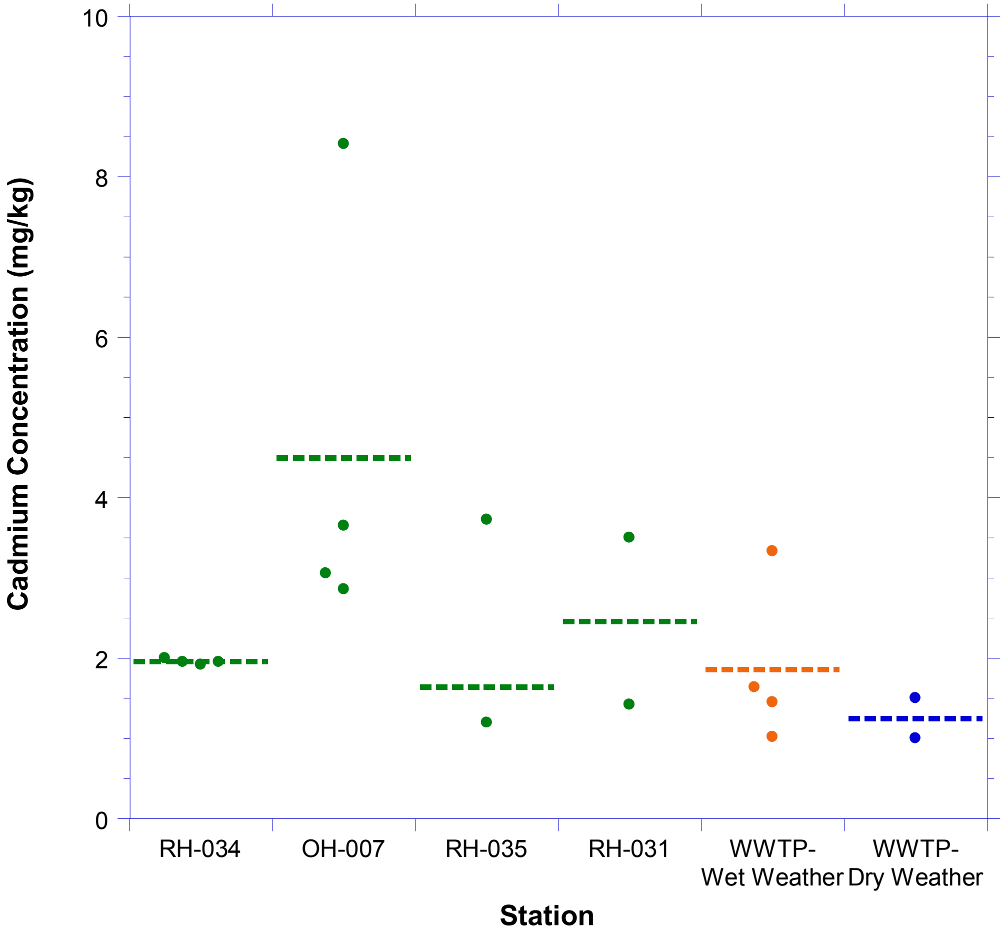
Figure A1-30

April 2013

Cadmium Whole Water Concentration from CSO and WWTP



Cadmium Concentration onSolids from CSO and WWTP



	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	0.45	0.91	0.41	0.50	0.33	0.24
SE ug/L	0.13	0.37	0.17	0.08	0.09	0.03

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	1.96	4.49	2.46	2.46	1.86	1.25
SE mg/kg	0.02	1.32	1.27	1.04	0.51	0.25

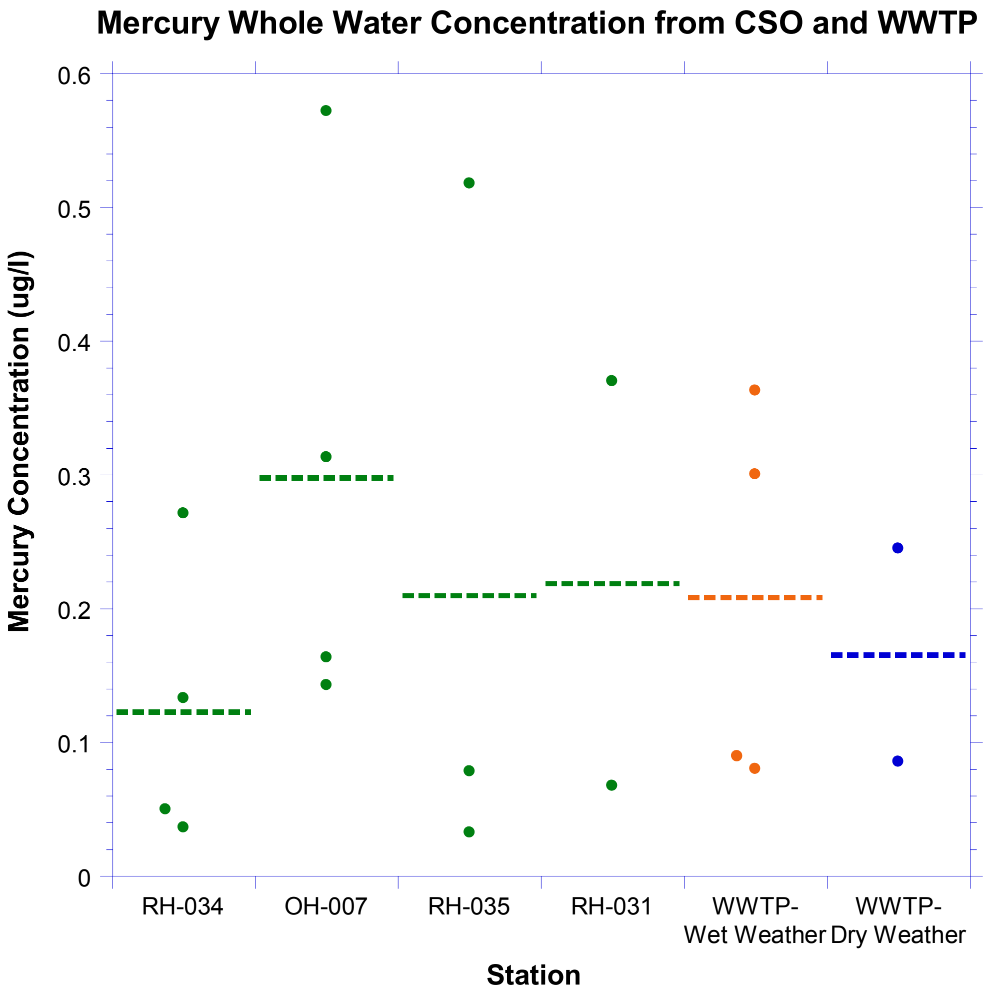
Environmental Protection

Cadmium Concentration in CSO and WWTP

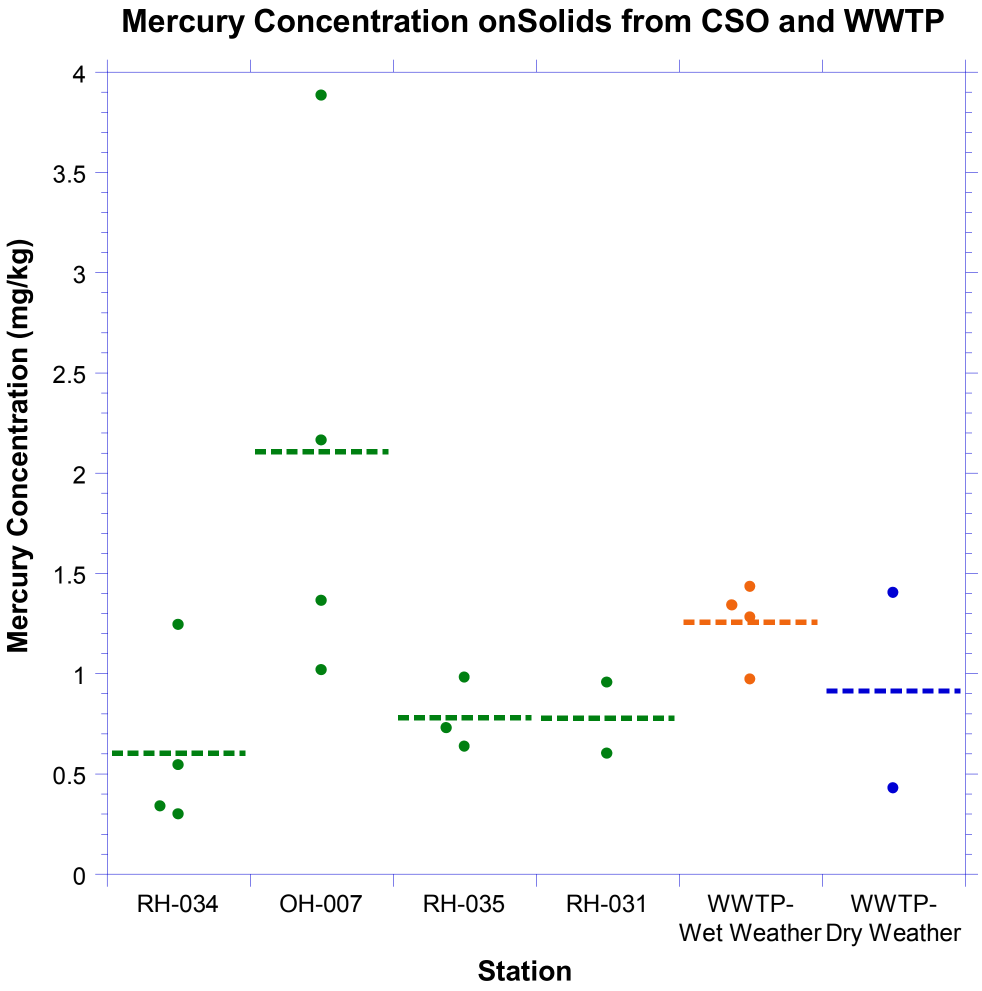
Gowanus Canal Superfund Site

Figure A1-31

April 2013



Mercury Whole Water Concentration from CSO and WWTP



Mercury Concentration onSolids from CSO and WWTP

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	0.12	0.30	0.21	0.22	0.21	0.17
SE ug/L	0.05	0.10	0.15	0.15	0.07	0.08

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	0.61	2.11	0.78	0.78	1.26	0.91
SE mg/kg	0.22	0.64	0.10	0.18	0.10	0.49

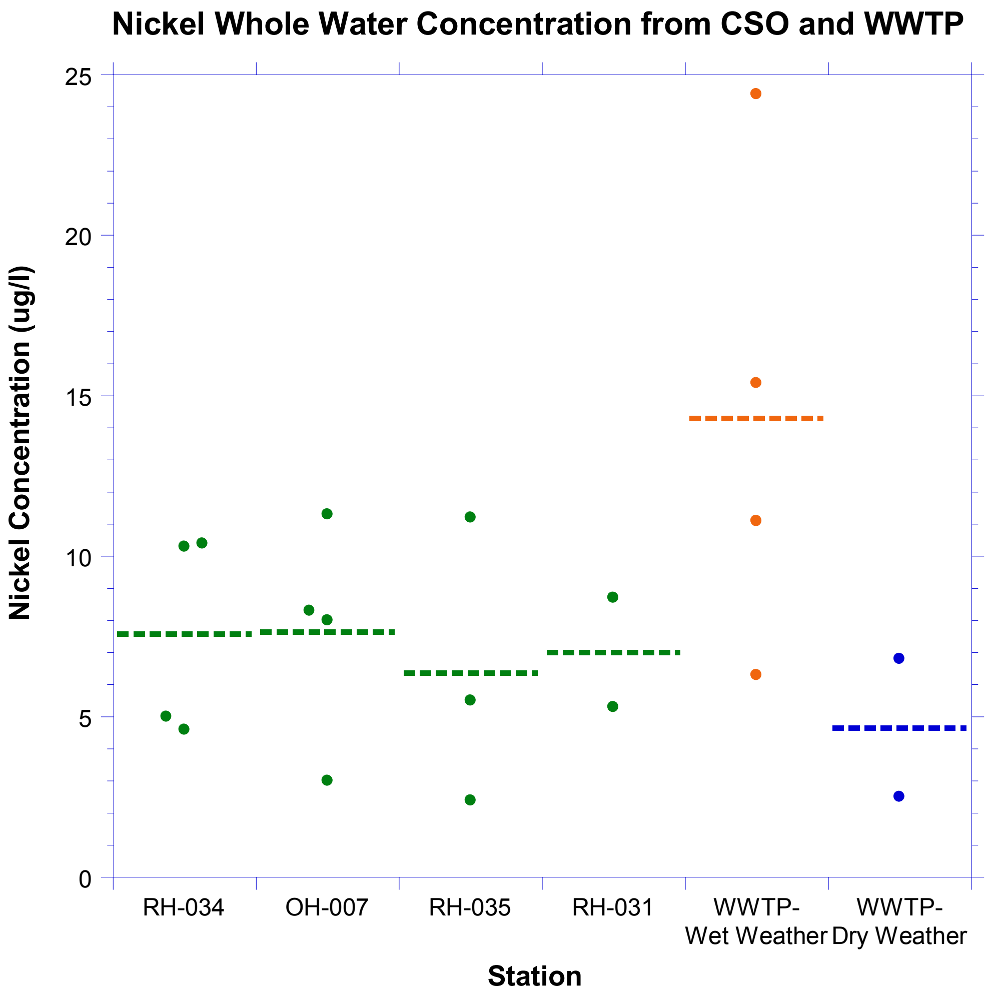
Environmental Protection

Mercury Concentration in CSO and WWTP

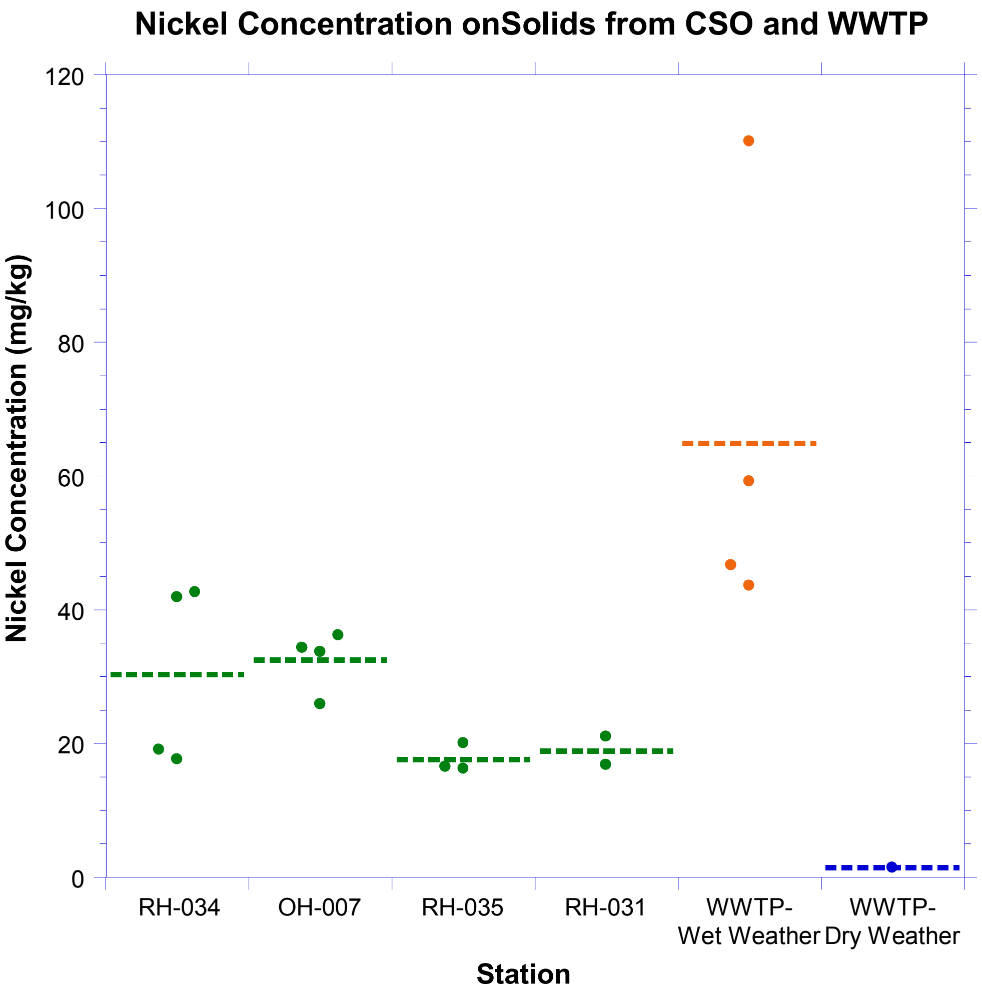
Gowanus Canal Superfund Site

Figure A1-32

April 2013



Nickel Whole Water Concentration from CSO and WWTP



Nickel Concentration onSolids from CSO and WWTP

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	7.6	7.7	6.4	7.0	14.3	4.7
SE ug/L	1.6	1.7	2.6	1.7	3.8	2.2

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	30.3	32.5	17.6	18.9	64.9	1.4
SE mg/kg	6.9	2.3	1.2	2.1	15.4	

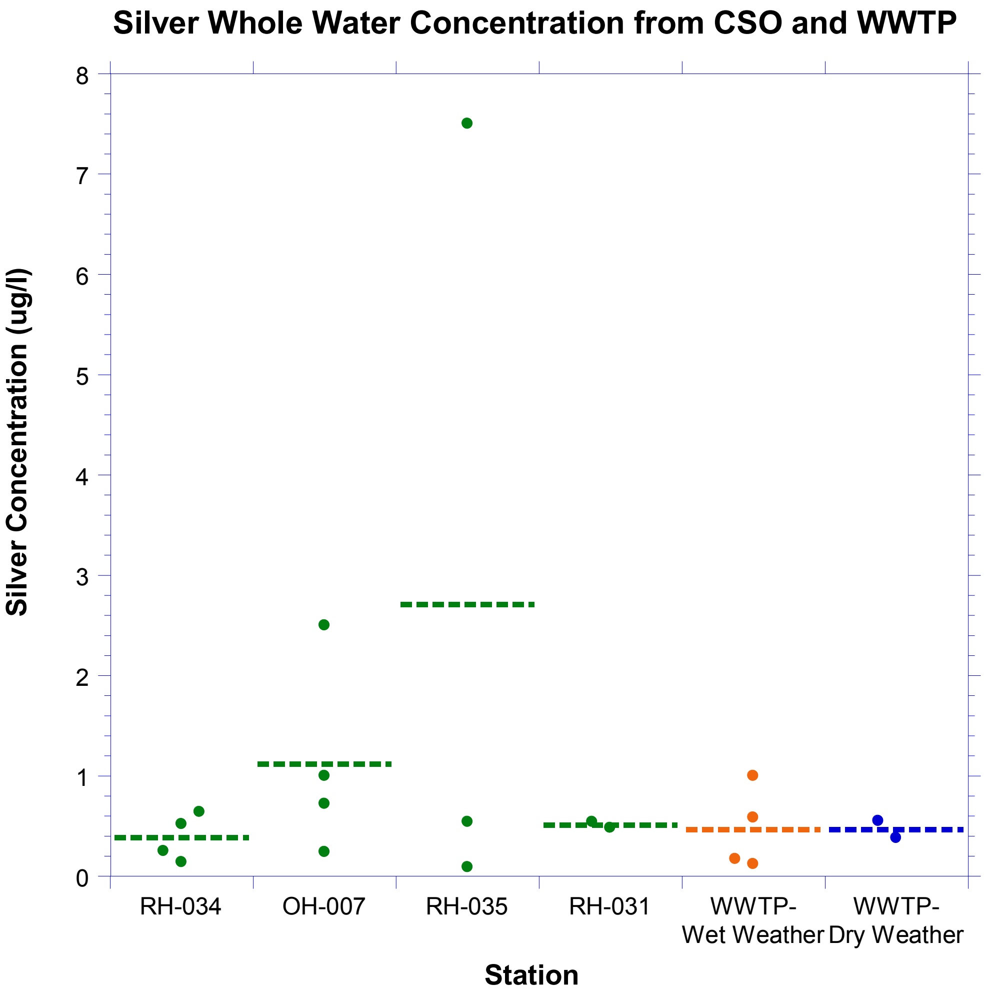
Environmental Protection

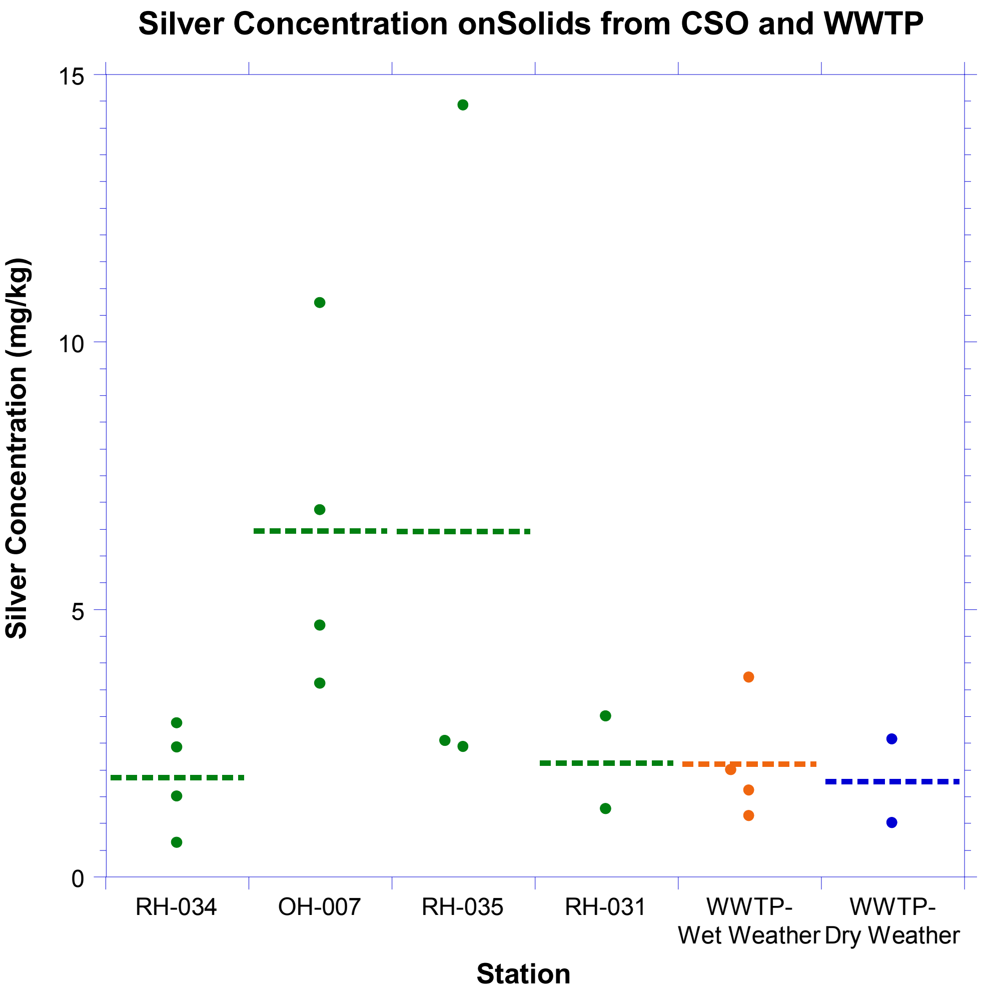
Nickel Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-33

April 2013





	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average ug/L	0.39	1.12	2.71	0.51	0.47	0.47
SE ug/L	0.12	0.49	2.40	0.03	0.21	0.09

	RH - 034	OH - 007	RH - 035	RH - 031	WWTP - WW	WWTP - DW
Average mg/kg	1.9	6.5	6.5	2.1	2.1	1.8
SE mg/kg	0.5	1.6	4.0	0.9	0.6	0.8

NYC Environmental Protection

Silver Concentration in CSO and WWTP

Gowanus Canal Superfund Site

Figure A1-34

April 2013

Appendix A2 – Surface Water Data Summary Report

Table of Contents

A2. Surface Water Data Summary Report

A2-1. Summary of the Surface Water Sampling Program

The City of New York (NYC)'s review of the EPA's surface water samples have raised several concerns about the utility of the EPA's surface water data set. These concerns include:

1. The EPA's surface water samples were collected from a depth of 6 inches below the water surface, which is not representative of the bulk water column conditions because of the potential for contaminants to volatilize from the water surface or for the sample to incorporate surface sheens.
2. Although dry weather samples did not have a collection criteria related to tide, wet weather samples were collected following low tide. Tide cycles play a critical role in the discharge of groundwater and the flux of contaminants from the sediment, and there is less water in the Canal for dilution during low tide. For these reasons, it is expected that contaminant levels will be at their highest during low tides. However, the two highest Total Polycyclic Aromatic Hydrocarbons (PAHs) results from the EPA's data set are from dry weather samples. Because the dry weather sampling was not tidally constrained and the wet weather sampling was, the results are not directly comparable.
3. Detection limits used for PAHs by the EPA were too high to discern the levels of contaminants in the Canal.

These concerns make the EPA's data set inadequate for the investigation of sources of contaminants in the Canal or for characterizing the distribution of contaminants in the surface water of the Canal. They also negate the comparison of wet weather to dry weather conditions in the Canal. Based on these concerns, the City concluded that the appropriate means of assessing inputs to the Canal's water column during dry weather would be to collect a tidally constrained (low tide) representative data set, analyzed with detection limits that are low enough so that contaminant patterns in the Canal can be discerned.

Surface water sampling activities were conducted in the Canal, and the Gowanus Bay between February 6 and March 6, 2013. A total of 23 locations were sampled, 18 within the Canal (SW-1 to SW-15, TB-1 to TB-3) and 5 in the Gowanus Bay (reference sample locations SW-1Ref to SW-5Ref). These locations are shown in Figure A2.1-1. Additionally, field duplicates, equipment blanks and trip blanks were collected for quality assurance/quality control protocols.

Surface water sampling was conducted using an established set of protocols (see Louis Berger & Associates, PC, 2013) that have been summarized below. Each proposed sampling location was located approximately 500 feet apart in the center of the Canal beginning at the mouth of the Canal and moving upstream towards the head of the Canal. Fifteen sample locations were located within the main stem of the Canal and three sample locations (TB-1 to TB-3) were located within turning basins offset from the Canal as shown in Figure A2.1-1.

Surface water sampling was conducted from the deck of a 32-foot jet-propelled boat (The Anthony Miller) and a small approximately 14-foot "jon" (flat bottom) boat. The Anthony Miller was used for the majority of the sampling activities due to its small draft (2 feet), maneuverability and lower potential for sediment disturbance as compared to a propeller driven boat. Where draft or other access issues (low bridges or other in-Canal obstructions) precluded the use of the jet boat, a propeller driven "jon" boat was used to access sample locations. Samples were collected above the 3rd Avenue Bridge using the "jon" boat due to bridge damage from Hurricane Sandy which prevented the bridge from opening. Sample collection using the Anthony Miller was conducted after the engine had been turned off and exhaust fumes were allowed to dissipate. Sampling was carried out upwind of the exhaust and at the opposite end of the boat to the exhausts. When sampling occurred using the "jon" boat, the boat was anchored and the engine turned off before sampling was conducted. Any sediment disturbed was allowed to settle/dissipate as much as practical before sampling occurred.

Sampling was conducted during a 6-hour window bracketing low tide in the Canal. This sampling window was used to ensure that water sampled from the Canal would contain the maximum influence of water discharging to the Canal from the sediment-water interface and avoid having this influence diluted by incoming tidal flow. At each sample location, the sample point was located using real time differential GPS to within an approximate 10-foot radius of the target location. The boat was held stationary by either by anchoring in the Canal or tied to a stationary object (bridge abutment/pier). Once anchored, the boat engine was turned off to reduce the possibility of contamination from engine exhaust and sediment disturbance. A GPS measurement was taken once the boat was stationary to determine actual sample location and later recorded in a bound field notebook.

Once on-station, a YSI Model 600XL Multi Sonde with Handheld 650 display was used to determine the total depth of the water column. In the few instances, when the YSI sonde pressure transducer was not working properly, a fiberglass meter tape was affixed to the sonde and the depths manually measured. The YSI 600 XL provided measurement of the following parameters: dissolved oxygen (DO), pH, temperature, conductivity, total dissolved solids (TDS), specific conductance, resistivity, salinity, oxidation reduction potential (ORP) and depth. Water quality measurements were collected at one-foot intervals beginning at a depth of one foot below water surface to the bottom of the Canal. In instances where the water was shallow, smaller measurement intervals were used to adequately profile the water column. All measurements were recorded in a bound field book. A series of graphs showing conductivity with depth is included as Figures A2.1-2a through A2.1-2d.

After the water column was profiled using the YSI, surface water samples were collected for the following analyses: PAHs (whole water and dual phase), total petroleum hydrocarbons – diesel range organics (TPH-DRO) and DRO extractables, total petroleum hydrocarbons – gasoline range organics (TPH-GRO), volatile organic compounds (VOCs), metals (including mercury), total suspended solids (TSS), dissolved organic carbon (DOC) and particulate organic carbon (POC). The results for total suspended solids concentrations are summarized in **Table A2.1-1** below. Note that the suspended solids concentrations in the Canal are similar to those observed in Gowanus Bay. Additionally, no consistent differences were observed between top and bottom water samples.

Table A2.1-1 – Total Suspended Solids

Sample ID	Sample Horizon	Location	TSS (mgL)
NYCDEP-SW-1	Bottom	Canal	32
NYCDEP-SW-1	Top	Canal	23
NYCDEP-SW-2	Bottom	Canal	24
NYCDEP-SW-2	Top	Canal	37
NYCDEP-SW-3	Bottom	Canal	26
NYCDEP-SW-3	Top	Canal	21
NYCDEP-SW-4	Bottom	Canal	34

Sample ID	Sample Horizon	Location	TSS (mgL)
NYCDEP-SW-4	Top	Canal	28
NYCDEP-SW-5	Bottom	Canal	71
NYCDEP-SW-6	Bottom	Canal	35
NYCDEP-SW-6	Top	Canal	32
NYCDEP-SW-7	Bottom	Canal	35
NYCDEP-SW-7	Top	Canal	57
NYCDEP-SW-8	Bottom	Canal	30
NYCDEP-SW-9	Bottom	Canal	23
NYCDEP-SW-9	Top	Canal	23
NYCDEP-SW-9 -Dup	Top	Canal	22
NYCDEP-SW-10	Top	Canal	22
NYCDEP-SW-11	Top	Canal	22
NYCDEP-SW-12	Bottom	Canal	28
NYCDEP-SW-12	Top	Canal	32
NYCDEP-SW-13	Top	Canal	33
NYCDEP-SW-14	Top	Canal	32
NYCDEP-SW-15	Top	Canal	31
NYCDEP-SW-15-Dup	Top	Canal	25
NYCDEP-SW-TB-1	Top	Turning Basin	25
NYCDEP-SW-TB-2	Top	Turning Basin	30
NYCDEP-SW-TB-3	Top	Turning Basin	25
NYCDEP-SW-REF-1	Bottom	Reference Area	32
NYCDEP-SW-REF-1	Top	Reference Area	20
NYCDEP-SW-REF-2	Bottom	Reference Area	56
NYCDEP-SW-REF-2	Top	Reference Area	22

Sample ID	Sample Horizon	Location	TSS (mgL)
NYCDEP-SW-REF3	Bottom	Reference Area	32
NYCDEP-SW-REF3	Top	Reference Area	32
NYCDEP-SW-REF-4	Bottom	Reference Area	46
NYCDEP-SW-REF-4	Top	Reference Area	20
NYCDEP-SW-REF-5	Bottom	Reference Area	26
NYCDEP-SW-REF-5	Top	Reference Area	41
NYCDEP-SW-FIELD BLANK1	---	---	0.69

VOC samples were collected first using a small disposable Teflon® weighted bailer (1.6" OD X 12" long). After VOC collection, Teflon®-lined polyethylene tubing was attached to the YSI sonde and cable at appropriate depths (using Zip ties) to collect water samples. The depth of the bottom collection point was determined by the depth of the water column. If the total depth of the water column was 7 feet or less, only one sample was collected at the mid depth of the Canal. Otherwise, in 8 feet or more of water, the top sample was at 2 feet below the surface and the bottom sample was at 2 feet above the sediment water interface. The sonde cable was weighted to counteract drift and ensure that samples were collected from the correct depth.

After purging the sample line(s) using a peristaltic pump, the mercury sample was then collected using “clean hands” protocols as described in the standard operating procedure (SOP). All other sample containers were then filled. When two samples were to be collected from one location (top and bottom), both samples were collected simultaneously using two peristaltic pumps. All samples were placed on ice in a cooler for sample management and subsequent daily shipping with appropriate trip and temperature blanks. PAH samples were shipped to AXYS Analytical Serves Ltd. in Surrey, British Columbia while the remaining samples were shipped to Kathadin Analytical Services, Inc. in Maine. The following table shows the sample collection dates.

Table A2.1-2 - Sample Collection Dates

Sample ID	Date	Sample ID	Date
SW-1	2/6/2013	SW-13	3/5/2013
SW-2	2/6/2013	SW-14	3/5/2013
SW-3	2/6/2013	SW-15	3/5/2013
SW-4	2/7/2013	SW-1Ref	2/19/2013
SW-5	2/7/2013	SW-2Ref	2/19/2013
SW-6	2/7/2013	SW-3Ref	2/6/2013

Sample ID	Date	Sample ID	Date
SW-7	2/7/2013	SW-4Ref	2/19/2013
SW-8	2/7/2013	SW-5Ref	2/19/2013
SW-9	2/18/2013	TB-1	3/5/2013
SW-10	2/18/2013	TB-2	3/5/2013
SW-11	2/18/2013	TB-3	3/6/2013
SW-12	3/4/2013	Field Blank	2/20/2013

The delays in sample collection were primarily weather-related, necessitating a 3-day delay between the end of the weather event and continuation of sampling. The weather events occurred on 1/31/2013 (rainfall), 2/8/2013 (rainfall), 2/20/2013 (sewage discharge into Canal), 2/23/2013 (rainfall) and 2/27/2013 (rainfall) (see **Figure A2.1-3**).

Delays were also required for coordinating sample collection with low tide occurrences during daylight hours resulting in resumption of sampling on 3/4/2013. Sampling was also not conducted on Fridays due to restrictions on sample shipments out of the US arriving at the receiving laboratory within sample holding times.

A comparison of analytical data for surface water samples collected by the City in 2013 and those collected by the EPA in 2010 for both PAHs and metals are shown in the following tables.

A review of Table A2.1-3 below indicates that the minimum PAH concentrations for samples collected by the City are generally one to two orders of magnitude lower than the EPA's detection limits. Similarly, EPA maximum values are generally higher than data collected by the City, but their averages are a function of their detection limits and not of actual concentrations in the Canal. The City employed a high-resolution, high sensitivity analytical method to analyze PAHs, so there are no non-detect values in NYC's data set. The average Total PAHs concentration from the City's sampling event is higher than the EPA's average Total PAHs concentration, indicating that the EPA data likely present an underestimate of the mass of PAHs found in the Canal. The EPA data set is largely comprised of sporadic detections of higher concentrations with mostly non-detect results. The EPA's highest concentrations are all from a few samples, mostly collected during the dry weather event and include samples from their reference areas. Overall, the City's surface water sampling event was completed successfully and provides a more sensitive, internally consistent and accurate data set that is better suited for to assess the level and distribution of contaminants found in the Canal.

Table A2.1-3 - Comparison of NYC DEP (2013) and EPA PAH Sample Data (2010)

Analyte	NYC				EPA				
	# of Samples	Min (ngl)	Max (ngl)	Avg (ngl)	# of Samples	Min (ngl)	Max (ngl)	Avg (ngl) *	Percent ND
2-Methylnaphthalene	38	4.44	1565	410	81	17J	3000	89.4	95%
Acenaphthene	38	3.03	4490	1017	81	ND = 100	940	232	43%
Acenaphthylene	38	1.34	227	68.2	81	ND = 100	ND =1000	-	100%
Anthracene	38	1.39	197	67.5	81	ND = 100	5200	157	95%
Benz[a]anthracene	38	1.83	51.3	18.4	81	ND = 100	940	96.3	85%
Benzo[a]pyrene	38	2.04	41.3	12.7	81	ND = 100	1400	106	86%
Benzo[b]fluoranthene	38	2.33	25.3	9.07	81	ND = 100	1300	168	43%
Benzo[e]pyrene	38	1.76	38.1	11.2	0	Not Analyzed			
Benzo[ghi]perylene	38	1.21	18.8	6.48	81	ND = 100	1500	252	48%
Benzo[j,k]fluoranthenes	38	1.74	30.2	10.4	81	37J	1400	95.2	74%
Chrysene	38	3.06	73.3	26.9	81	ND = 100	1100	117	74%
Dibenz[a,h]anthracene	38	0.22	5.17	1.63	81	ND = 100	190	60.4	93%
Fluoranthene	38	6.83	279	113	81	ND = 100	2300	242	34%
Fluorene	38	1.80	426	151	81	ND = 100	320	75.7	75%
Indeno[1,2,3-cd]pyrene	38	1.39	17.7	6.24	81	ND = 100	1100	184	40%
Naphthalene	38	6.78	3960	265	81	ND = 100	1400	80.6	90%
Phenanthrene	38	6.70	965	343	81	ND = 100	1400	122	67%
Pyrene	38	6.90	297	119	81	ND = 100	1500	154	62%
Total PAHs	38	61.00	8650	2660	70	-	13309	1866**	-

* - Uses ½ the detection limit to compute average

** - Does not include samples that were all non-detect (ND)

Min – Minimum

Max - Maximum

Avg - Average

ngl - nanograms per liter

ND - Non-Detect

J – Estimated value

References:

Louis Berger & Associates, PC. 2013. Quality Assurance Project Plan for Environmental Investigations at the Gowanus Canal Superfund Site.

A2-2. Evidence for Degradation of Naphthalene in the Gowanus Canal System

Naphthalene is the most prominent PAH component of the coal tar found beneath and adjacent to the Canal, and is the PAH with the highest concentration found in the groundwater and in the sediment. Figure A2.2-1 shows the percent proportion of Total PAHs represented by naphthalene and low molecular weight PAHs (LMW PAH) as compared to the Total PAHs concentration. As can be seen, the higher concentration samples are also the most rich in LMW PAH and in naphthalene (data is from GEI RI sediment data). However, in the shallow sediment, the proportion of PAHs represented by naphthalene decreases as the sediment-surface water interface is approached. Figure A2.2-2 shows the relative proportion of naphthalene and LMW PAHs with depth. As can be seen there is a gradient in both of these as the sediment surface is approached. The CSM prepared by CH2MHill for the EPA and presented in the RI states that groundwater and NAPL continue to discharge from the sediment (EPA, 2011). The EPA also describe the process for reducing the level of LMW PAH concentrations as compared to high molecular weight (HMW) PAH's:

> *The composition of a PAH mixture from a specific source changes after it enters a waterway due to a variety of weathering processes, including dissolution and biodegradation (decomposition by microorganisms).These processes preferentially reduce the proportion of two- and three-ring PAHs, thereby increasing the proportion of four- to six-ring PAHs over time (Boehm, 2006). The high-molecular-weight PAHs are resistant to degradation and tend to persist in the environment for long periods of time.*

However the EPA does not consider the implications of the degradation process with respect to groundwater and NAPL discharge, and only considers it as acting on PAHs in the water column (this language appears both in the RI and the Proposed Plan):

> *Contaminants with a higher solubility and volatility (i.e., VOCs and some of the low-molecular-weight SVOCs) tend to disperse in the water column. Therefore, the accumulation of soft sediments in the canal over time has resulted in the accumulation of high levels of persistent contaminants.*

As described in Comment 3 of the City's technical comments, there is significant evidence that groundwater and NAPL are the primary source of PAHs to the Canal, which is contrary to the EPA's assertion that contaminated sediment is accumulated from the water column. The process that is not considered by the EPA in the above statement is the loss of naphthalene from groundwater/NAPL based PAH load to the sediment. The loss of naphthalene from the groundwater load as the contamination approaches the surface water is a major factor in the composition of the total PAHs in the shallow sediment and is being mistaken for a process occurring in the water column.

It is important to recognize that of the PAHs, naphthalene is the simplest molecule, is 30 times more soluble than the next most soluble PAH, has the lowest particle affinity of the PAHs, and is the most easily biodegraded (ATSDR, 2005). Naphthalene can biodegrade both aerobically and anaerobically. Therefore, the most likely explanation for the depletion of naphthalene in the shallowest sediments is differences in the fate and transport properties and processes for naphthalene relative to the other PAHs.

Initial evidence for the degradation of naphthalene in the Canal is provided by the surface water samples obtained by the City. During the City's 2013 surface water sampling program, matched pairs of whole water and split phase samples (analyzed separately for dissolved and suspended matter-borne fractions) were collected at a limited number of stations. The "whole water" portion of samples were placed in laboratory-preserved bottles while samples that were to be analyzed for suspended and dissolved concentrations were put in containers that were preserved in the field. A comparison of the results of the measured whole water concentration and the sum of the dissolved and suspended matter-borne fractions was performed. Figure A2.2-3 shows the results of this analysis for naphthalene, acenaphthene, flourene and phenanthrene. As can be seen, only naphthalene shows large and systematic differences between the whole water concentration and the sum of the dissolved and suspended matter-borne fractions. In all but one instance, the field-preserved sample was greater than or equal to the lab-preserved sample. In contrast, the other PAH compounds did not exhibit similar poor agreement, indicative of similar losses. In most instances, the sample pair results agreed within 10 percent, as indicated by the two lines drawn parallel to the 1-to-1 line. These results indicate that naphthalene can rapidly degrade in a sample if not well preserved, since some samples with lab-applied preservative were not sufficiently well preserved to prevent naphthalene loss in the short time (typically seven days or less) between sample collection and processing at the lab. During this time, the samples were held at 4 C. By inference, it likely that such processes are also operating within the water column of the Canal, similarly degrading naphthalene in the water column,

Consistent with the premise that naphthalene is more biodegradable than the other PAH compounds, the City's initial surface water sampling results found that the distribution of naphthalene in the water column of the Canal is very different from that observed for other PAH compounds and that it appears that naphthalene is not conserved in the water column. Figure A2.2-4 shows the naphthalene concentrations in the Canal. As can be seen, naphthalene for the most part is at its highest concentration in the Canal bottom sample, when compared to the top sample at the same location. Figures A2.2-5, A2.2-6, A2.2-7 and A2.2-8, are the same presentations for acenaphthene, flourene, phenanthrene, and Total PAHs. As can be seen in these figures, the highest concentrations of these compounds and Total PAHs are generally found in the surface sample, with the exception at approximately 3500 feet from the head end of the Canal. The patterns for all four compounds are reversed here with the highest concentration found in the bottom sample, which may be indicative of groundwater discharge. Notably naphthalene shows a similar relationship between top and bottom samples at this location. Away from this location, however, the three other PAH compounds and Total PAHS all exhibit the same pattern with river mile and between top and bottom water samples. These results indicate that the same mechanism(s) are responsible for delivering and transporting all of these PAHs. As can be seen by comparing these figures, naphthalene clearly behaves differently. Given the rapid losses of naphthalene from the sample bottles described above, the different spatial distribution for naphthalene is likely due to degradation. The City notes that it is possible that the different behavior for naphthalene may be due to degradation in the bottle after collection and not in the water column. However, variations between matched pairs were no greater than six-fold (*e.g.* 10 *vs.* 60 ng/L for all but one of the pairs. In contrast water column naphthalene concentrations varied by more than 500-fold (*e.g.,* 10 *vs.* 5,000 ng/L) upstream of RM 0.2, whereas, for example, Total PAHs varied only 10 fold (*e.g.,* 10 *vs.* 100 ng/L) over the same distance. Based on this, the City concludes that naphthalene is not conservative and is subject to substantive water column degradation. Given the occurrence of this degradation in the water column, it is likely such degradation is taking place in the sediments as well.

Additional evidence for the loss of naphthalene from the sediments can be found in the discussion in Comment 5 of the City's technical comments. As described in detail there, the ratios among signature PAHs remain constant throughout the entire sediment column while, as shown in Figure A2.2-2, the ratio of naphthalene to Total PAH does not. Additionally, the ratios observed in surface sediments are highly correlated with MGP oils identified by National Grid and are significantly different from those observed on CSO solids. The double ratio plots presented in Comment 5 are insensitive to the presence of naphthalene so are an independent line of evidence tying surface sediments to deeper sediments and groundwater/NAPL as the source of contamination.

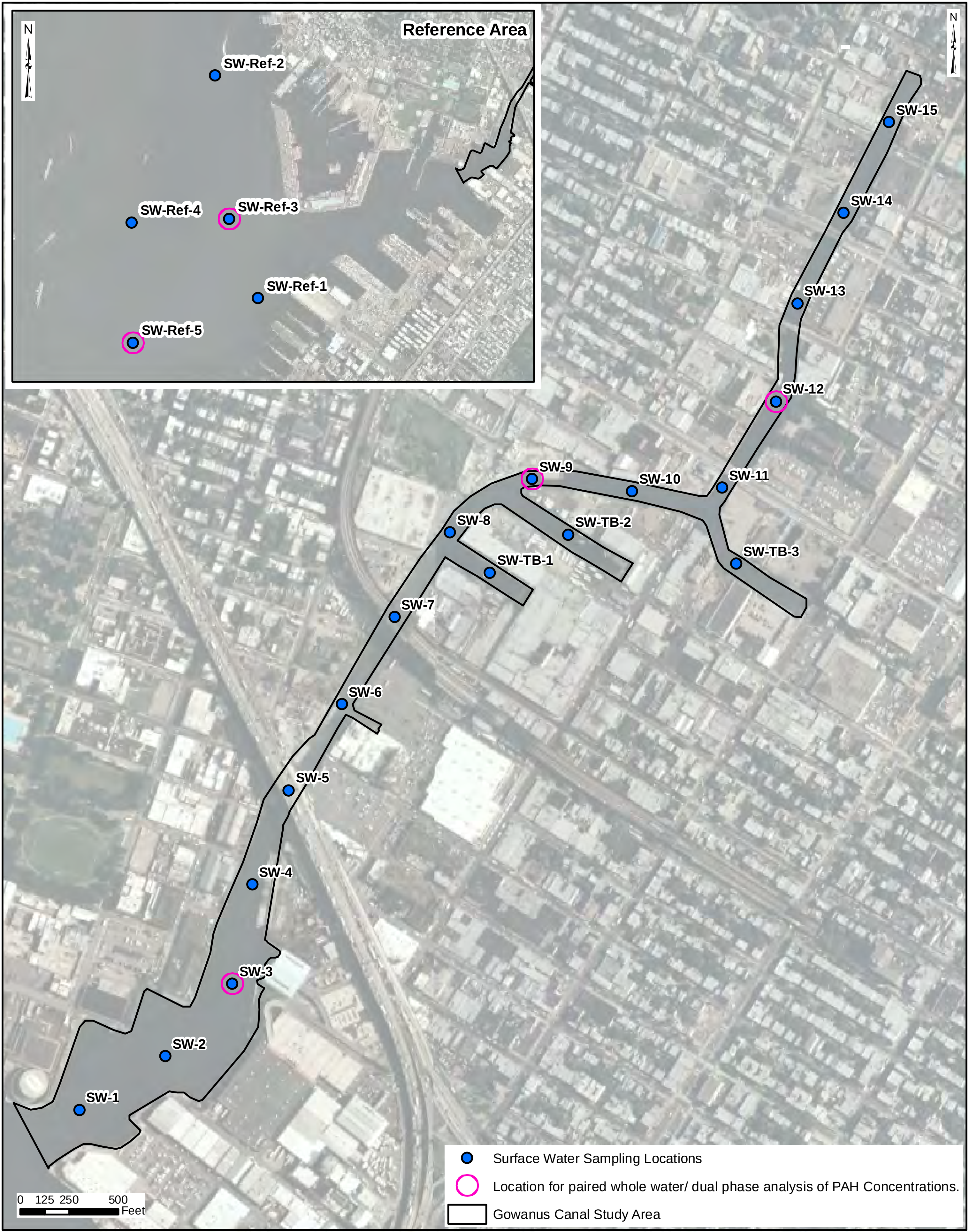
Based on these findings, the City concludes that naphthalene is not a conservative compound and is likely to biodegrade in the sediment and water column. For this reason, it is inappropriate to base comparisons of deeper sediment and shallow sediment simply on the ratio of LMW PAHs to high molecular weight (HMW) PAHs or to assume that contaminants in the surface sediment are derived solely from the water column. Different fate and transport processes affect each compound based on their own physiochemical properties. As described in Comment 3, if naphthalene is not included, the relative proportions of individual PAHs remain relatively consistent for LMW and HMW PAHs across the sediment column.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 2005. Toxicological profile for Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene. Atlanta, GA. U.S. Department of Health and Human Services, Public Health Service. August 2005.

Boehm, P.D. 2006. Polycyclic Aromatic Hydrocarbons (PAHs). In Environmental Forensics—Contaminant Specific Guide. R.D. Morrison and B.L. Murphy, eds. Elsevier Publishing.

EPA. 2011. Gowanus Canal Remedial Investigation Report. January 2011.



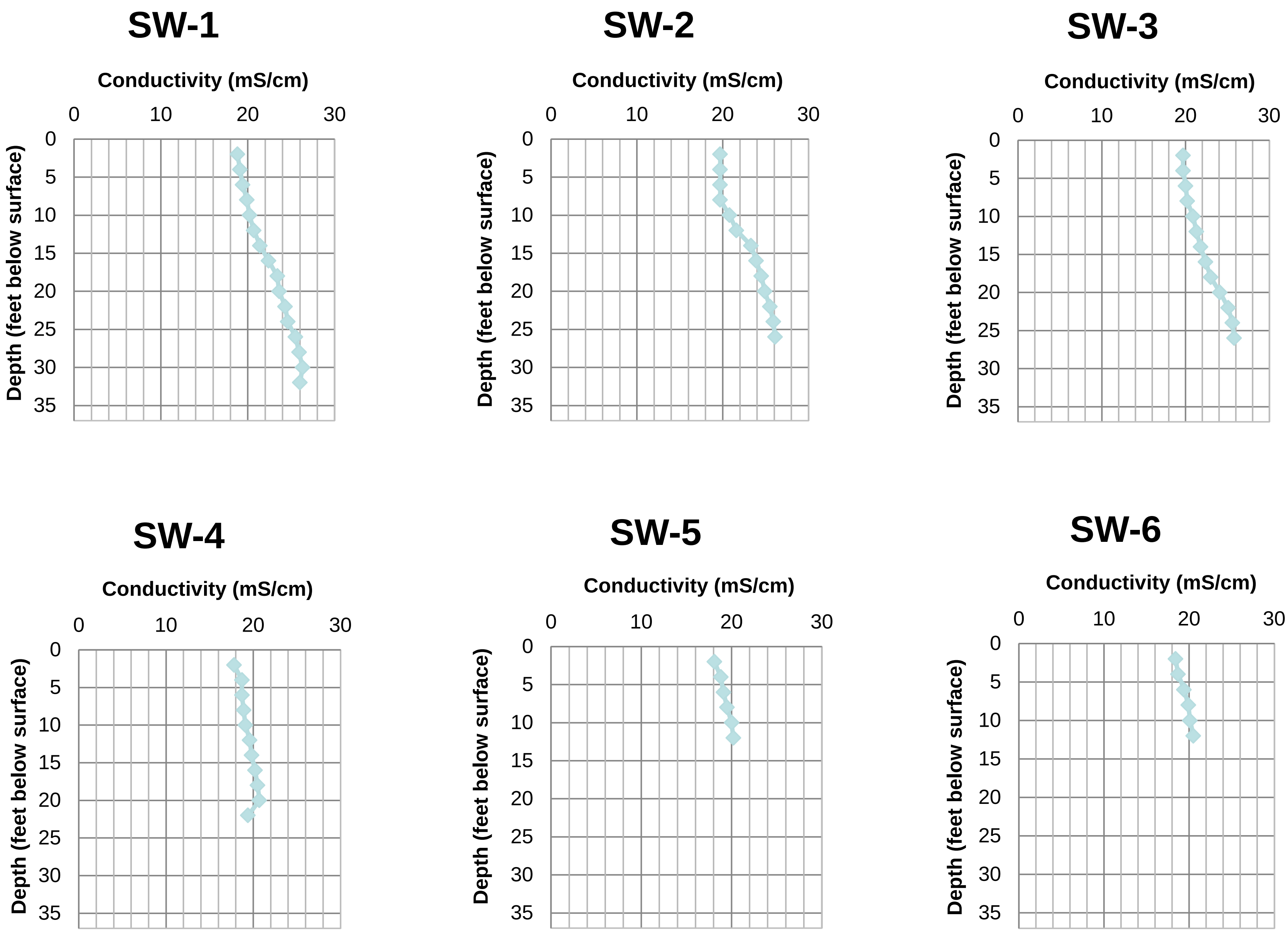
NYC Environmental Protection

Sampling Locations - Surface Water

Gowanus Canal Superfund Site

Figure A2.1-1

April 2013

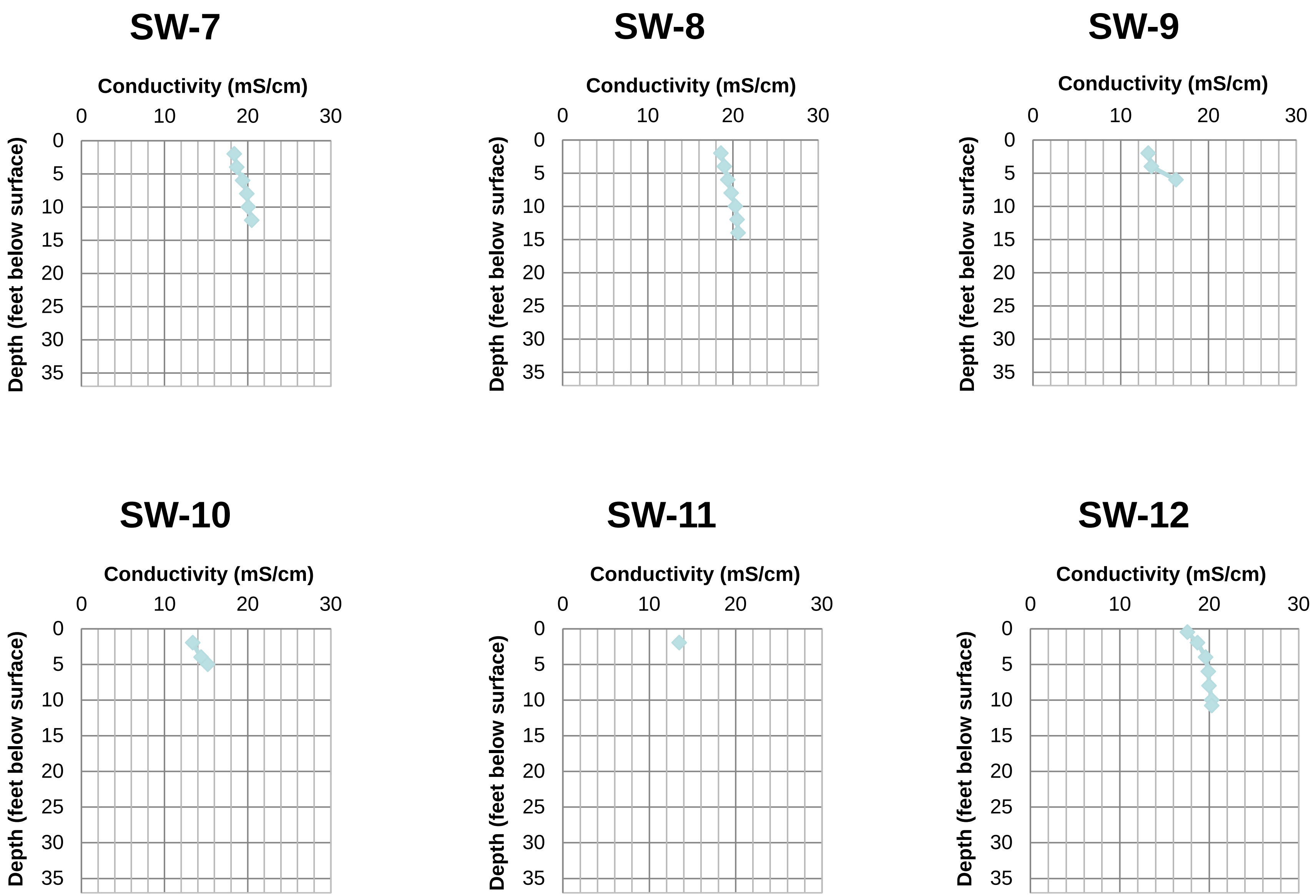


Water Column Salinity Profiles

Gowanus Canal Superfund Site

Figure A2.1-2a

April 2013



Environmental Protection

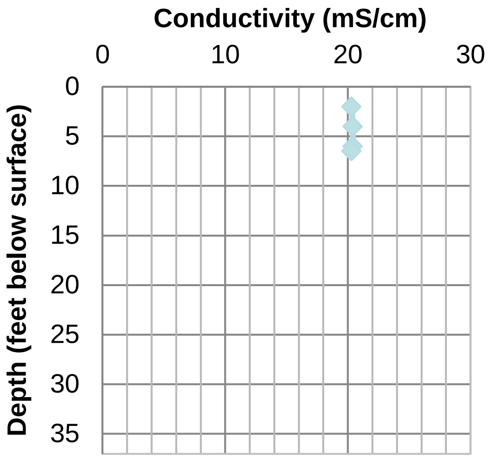
Water Column Salinity Profiles

Gowanus Canal Superfund Site

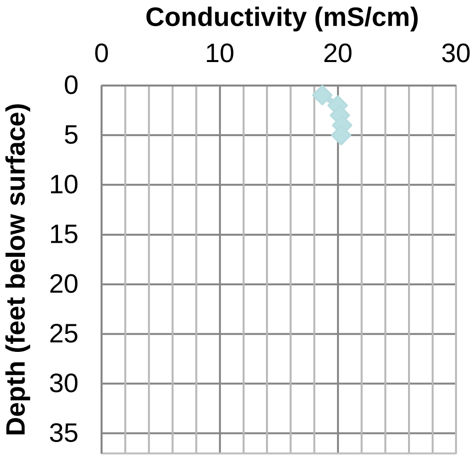
Figure A2.1-2b

April 2013

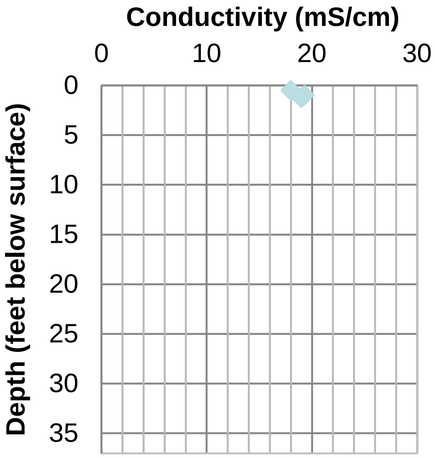
SW-13



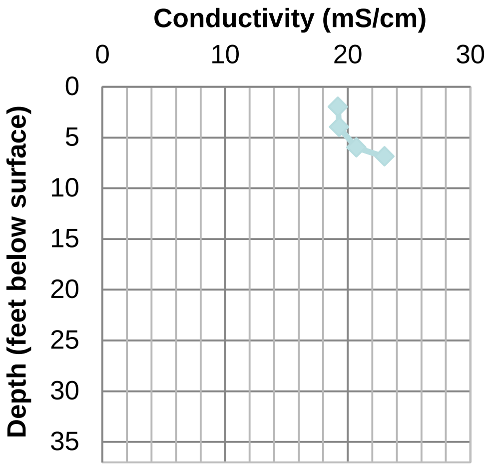
SW-14



SW-15



TB-1



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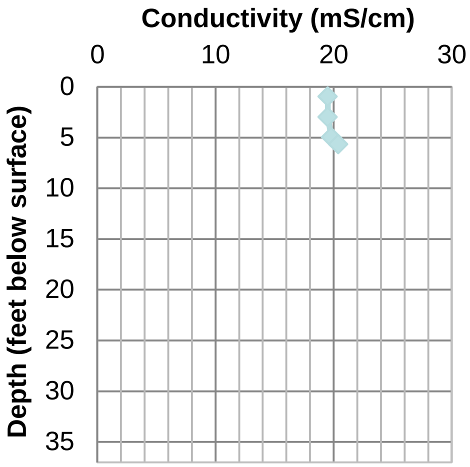

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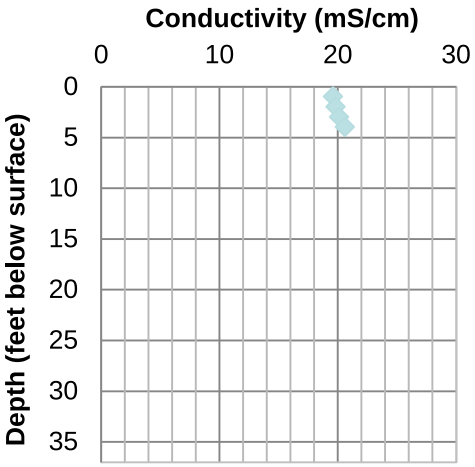


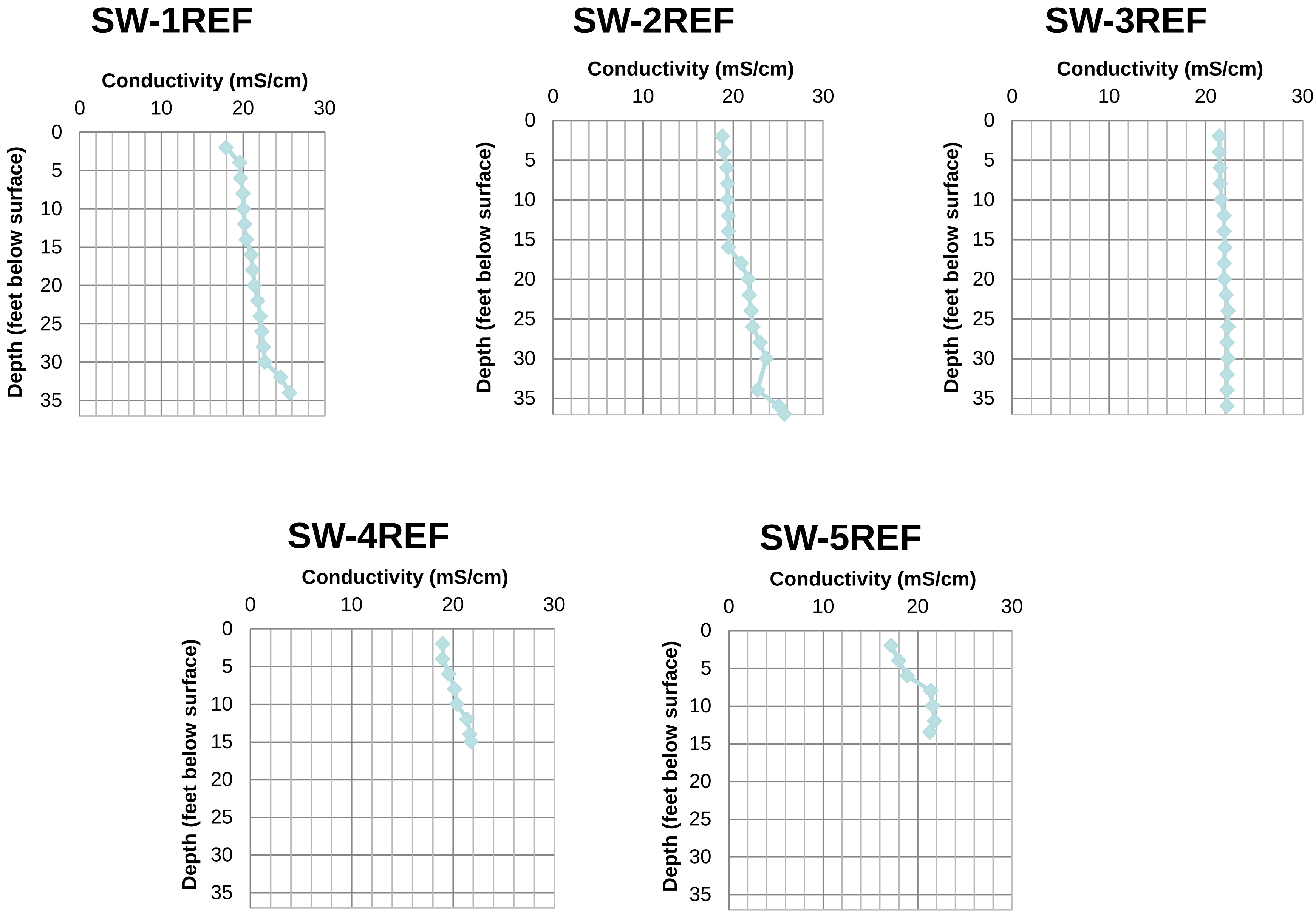
Environmental Protection

Water Column Salinity Profiles

Gowanus Canal Superfund Site

Figure A2.1-2c

April 2013



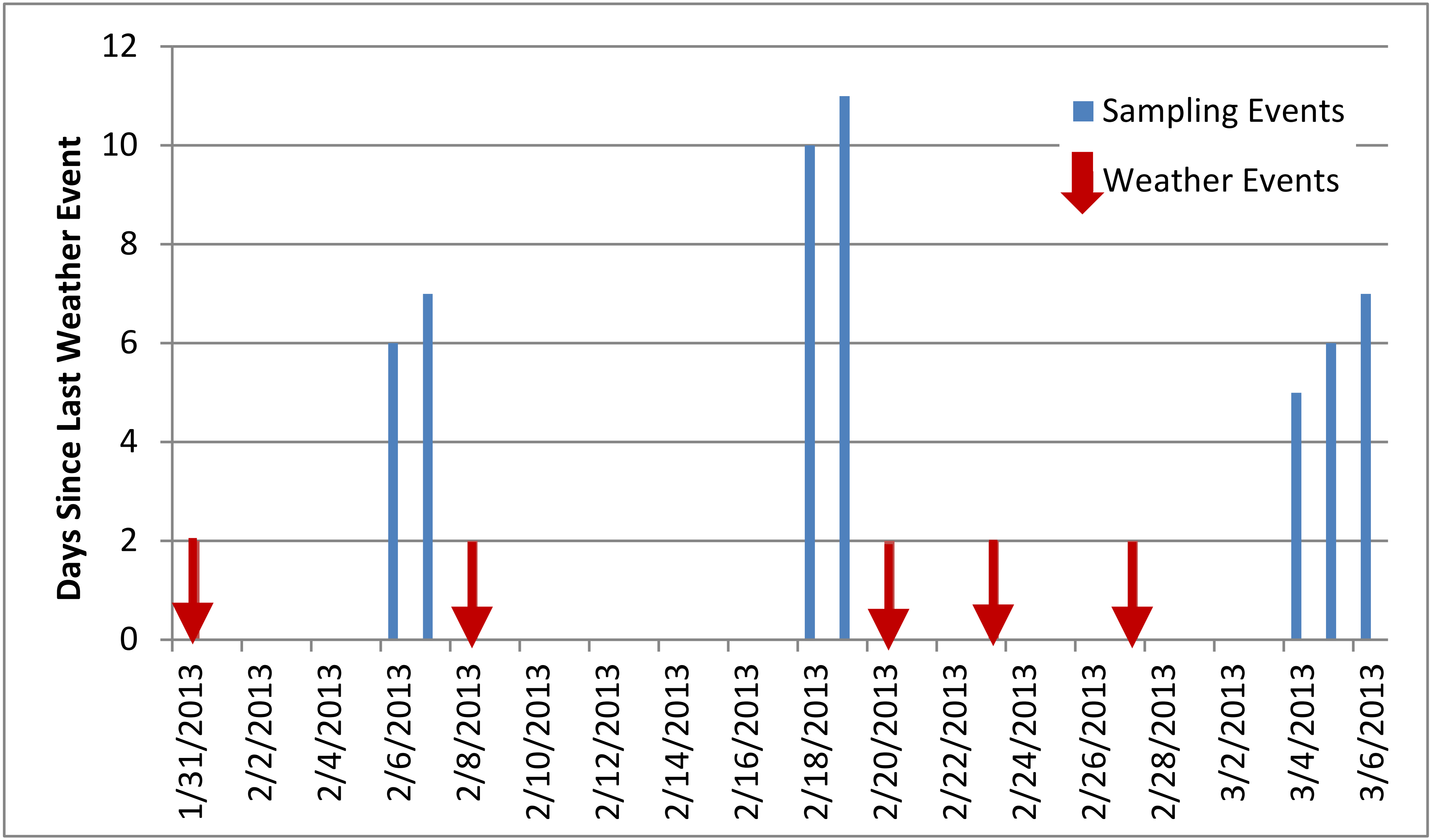
Environmental Protection

Water Column Salinity Profiles

Gowanus Canal Superfund Site

Figure A2.1-2d

April 2013



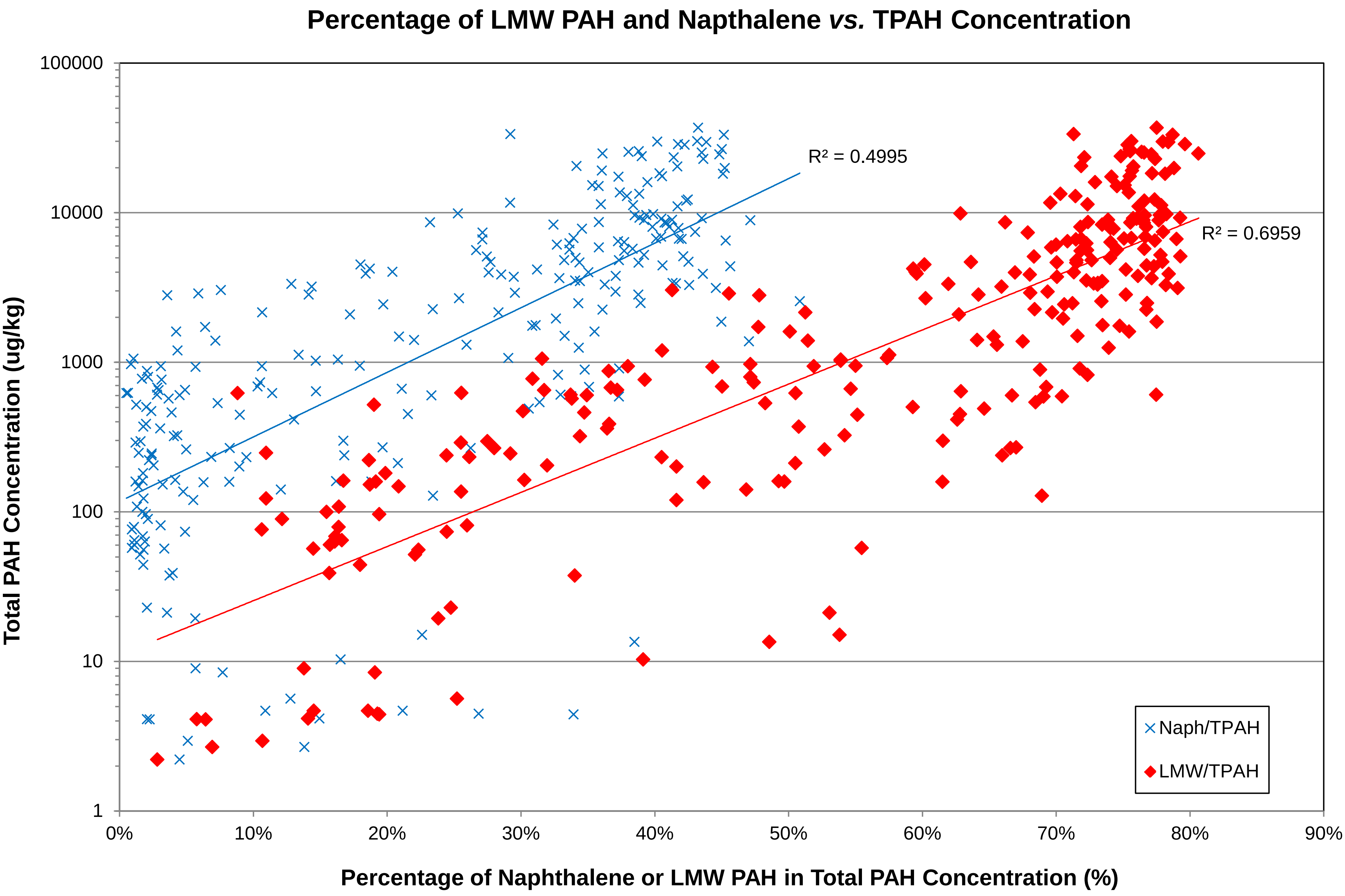
NYC Environmental Protection

NYCDEP Surface Water Sampling Timeline Showing Occurrence of Weather Events in Relation to Sample Collection Dates

Gowanus Canal Superfund Site

Figure A2.1-3

April 2013



Environmental Protection

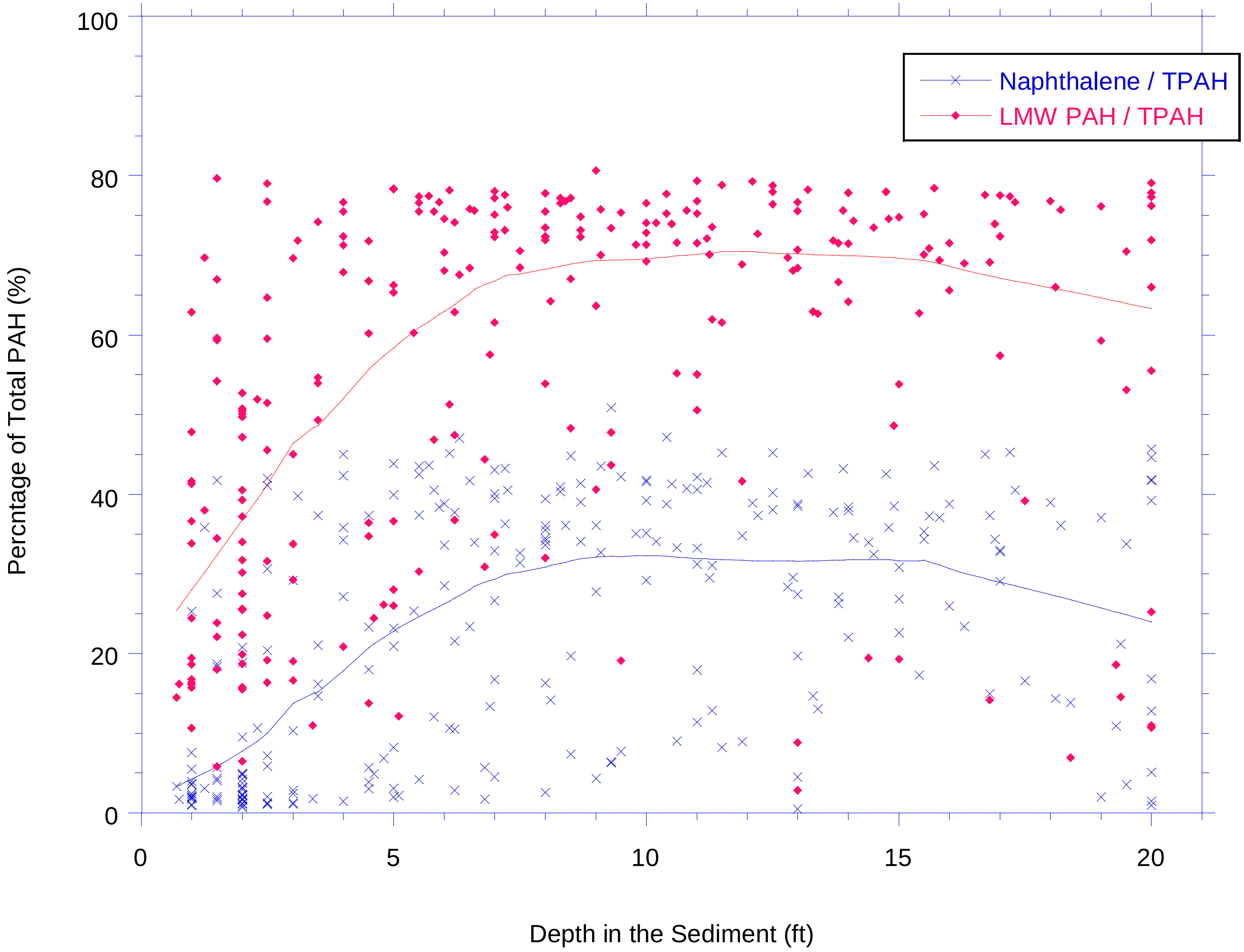
Percent LMW PAH and Naphthalene *vs.* TPAH Concentration

Gowanus Canal Superfund Site

Figure A2.2-1

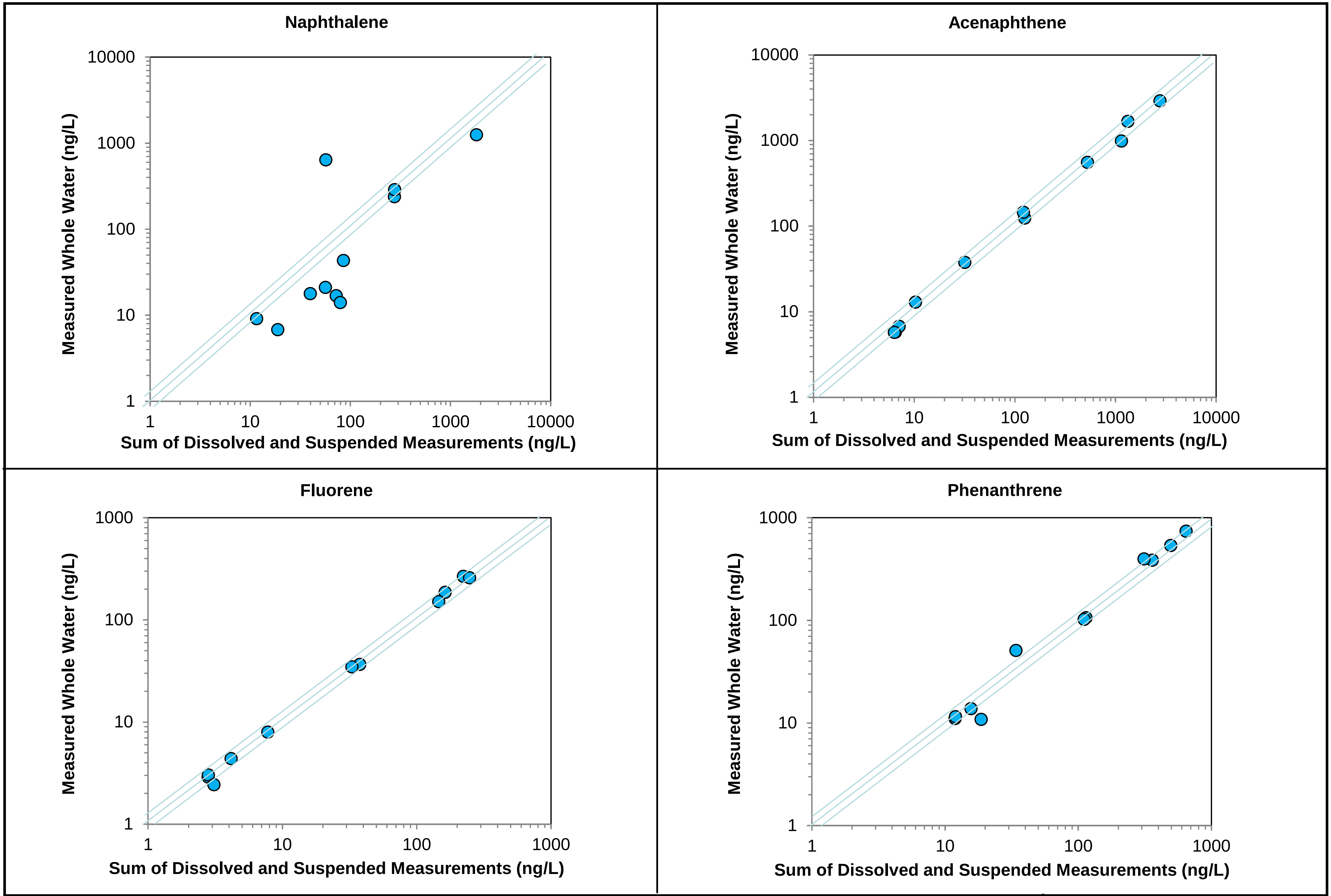
April 2013

LMW PAH and Naphthalene Percentage of Total PAH *vs.* Depth



Note: Lines represent weighted-average curves

NYC Environmental Protection	LMW PAH and Naphthalene Percentage of TPAH *vs.* Depth *Gowanus Canal Superfund Site*	Figure A2.2-2 April 2013

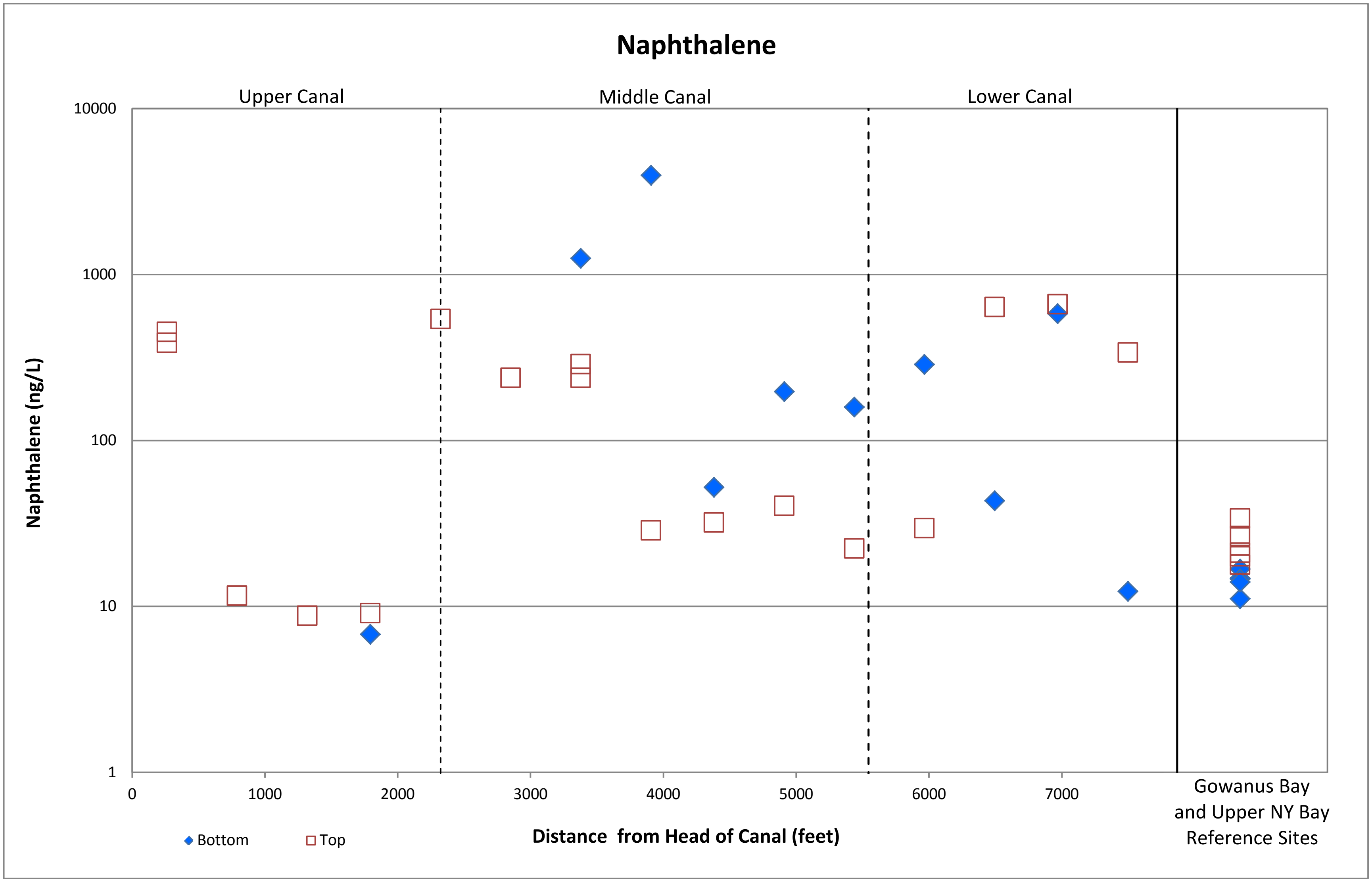


Comparison of Whole Water to
Sum of Dissolved and Suspended Fraction Measurements

Gowanus Canal Superfund Site

Figure A2.2-3

April 2013



Water Column Whole Water Concentrations – Naphthalene

Gowanus Canal Superfund Site

Figure A2.2-4

April 2013

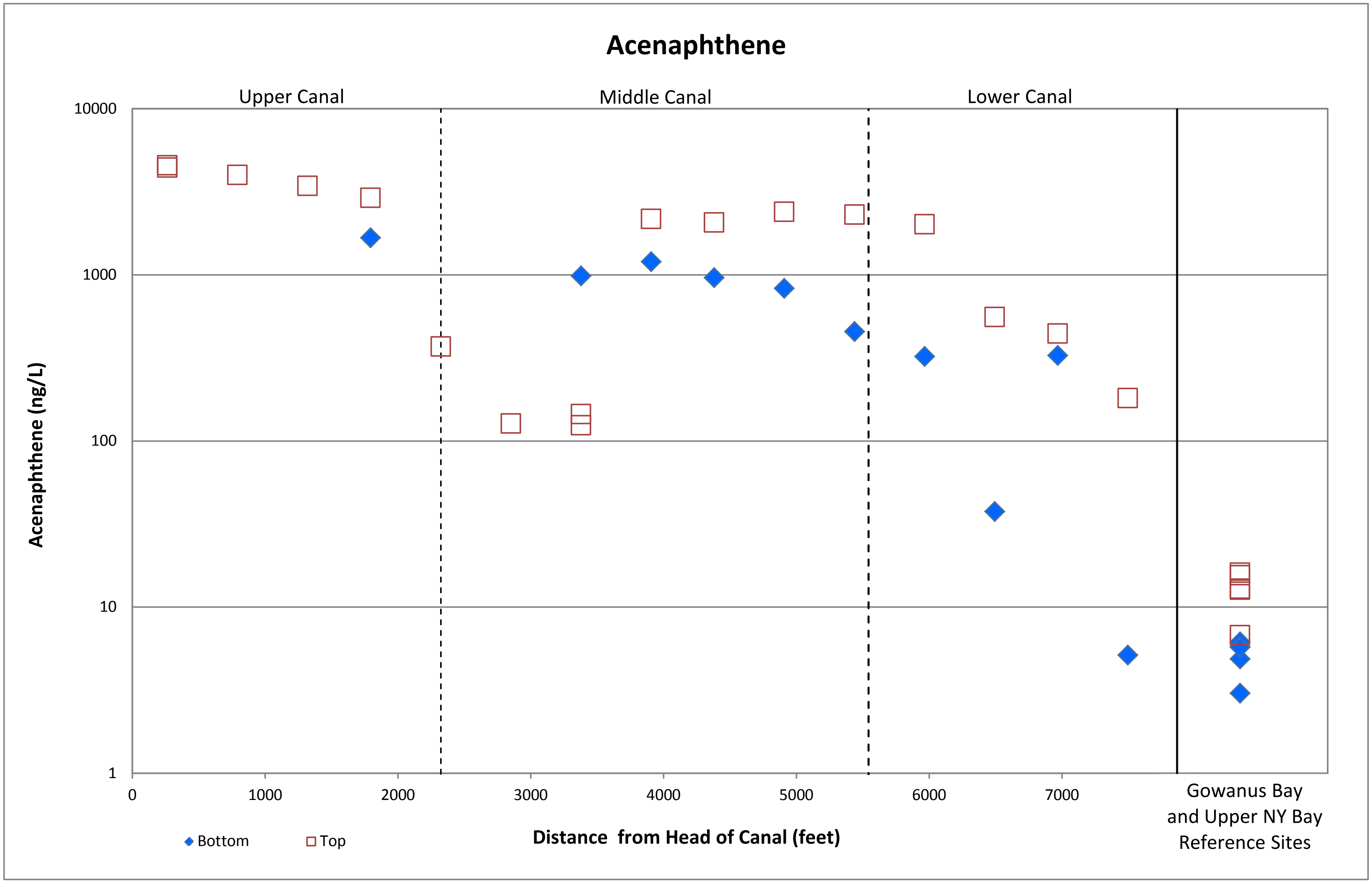
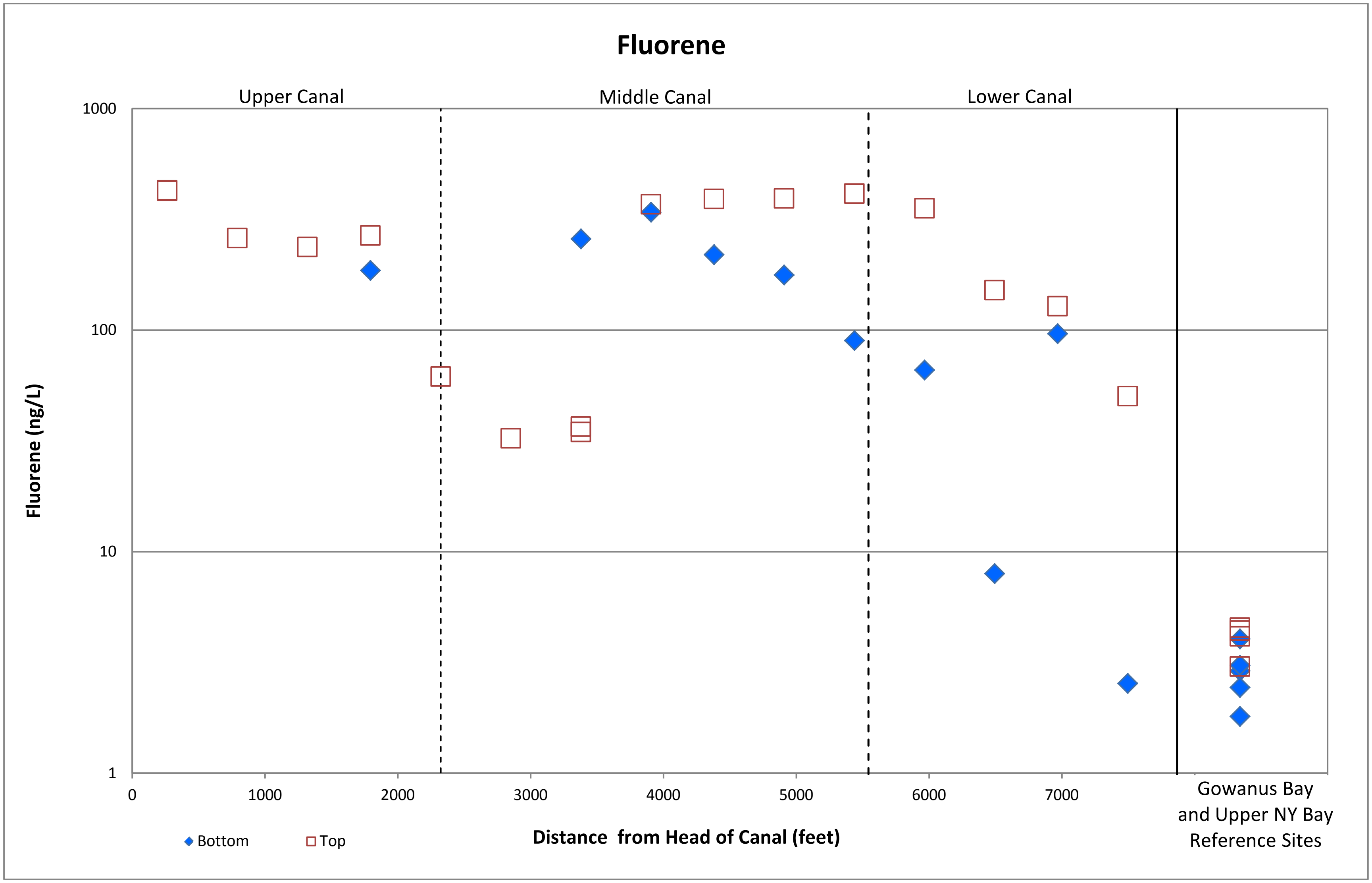


Figure A2.2-5

Water Column Whole Water Concentrations – Acenaphthene

Gowanus Canal Superfund Site

April 2013

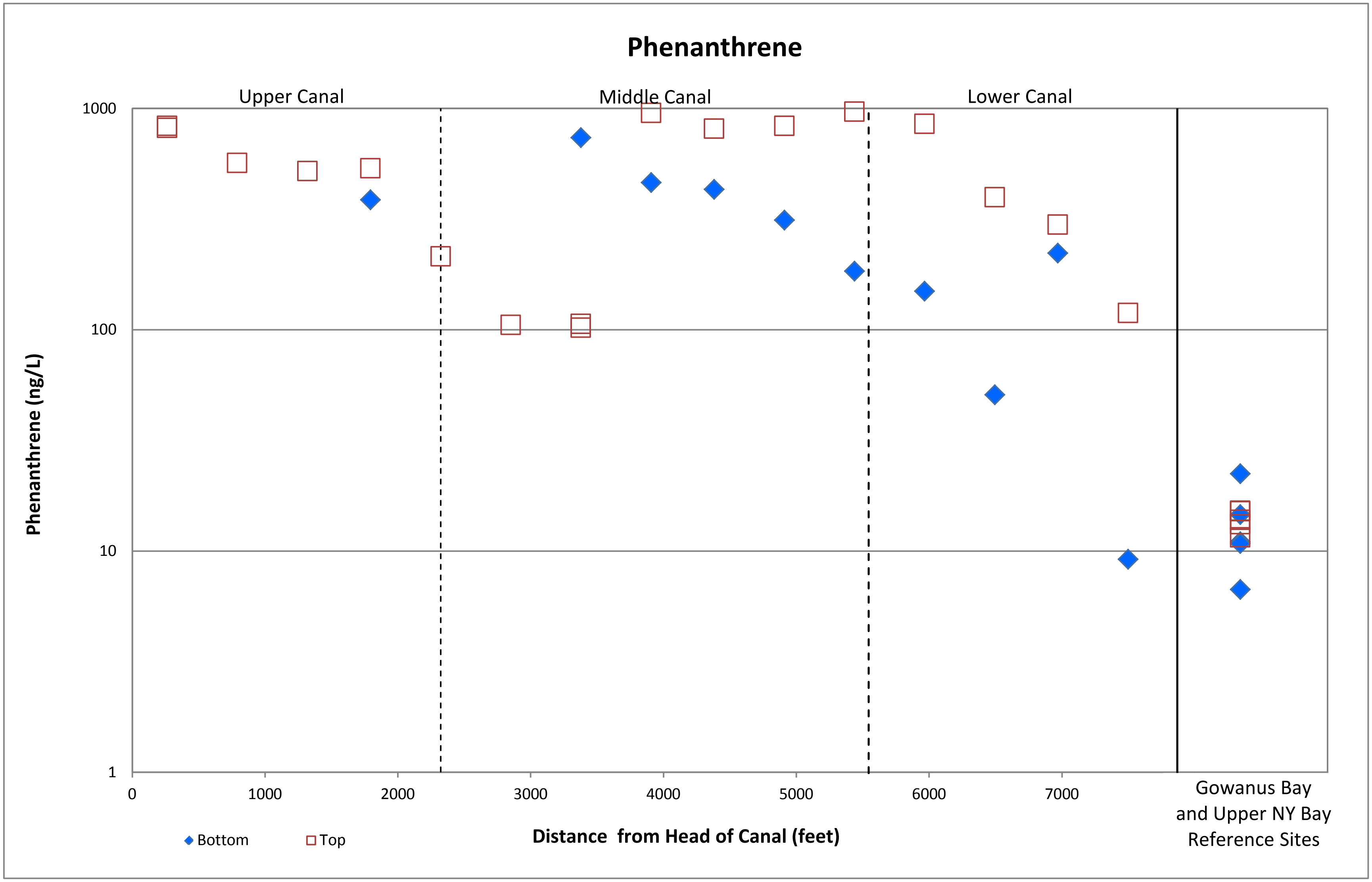


Water Column Whole Water Concentrations – Fluorene

Gowanus Canal Superfund Site

Figure A2.2-6

April 2013

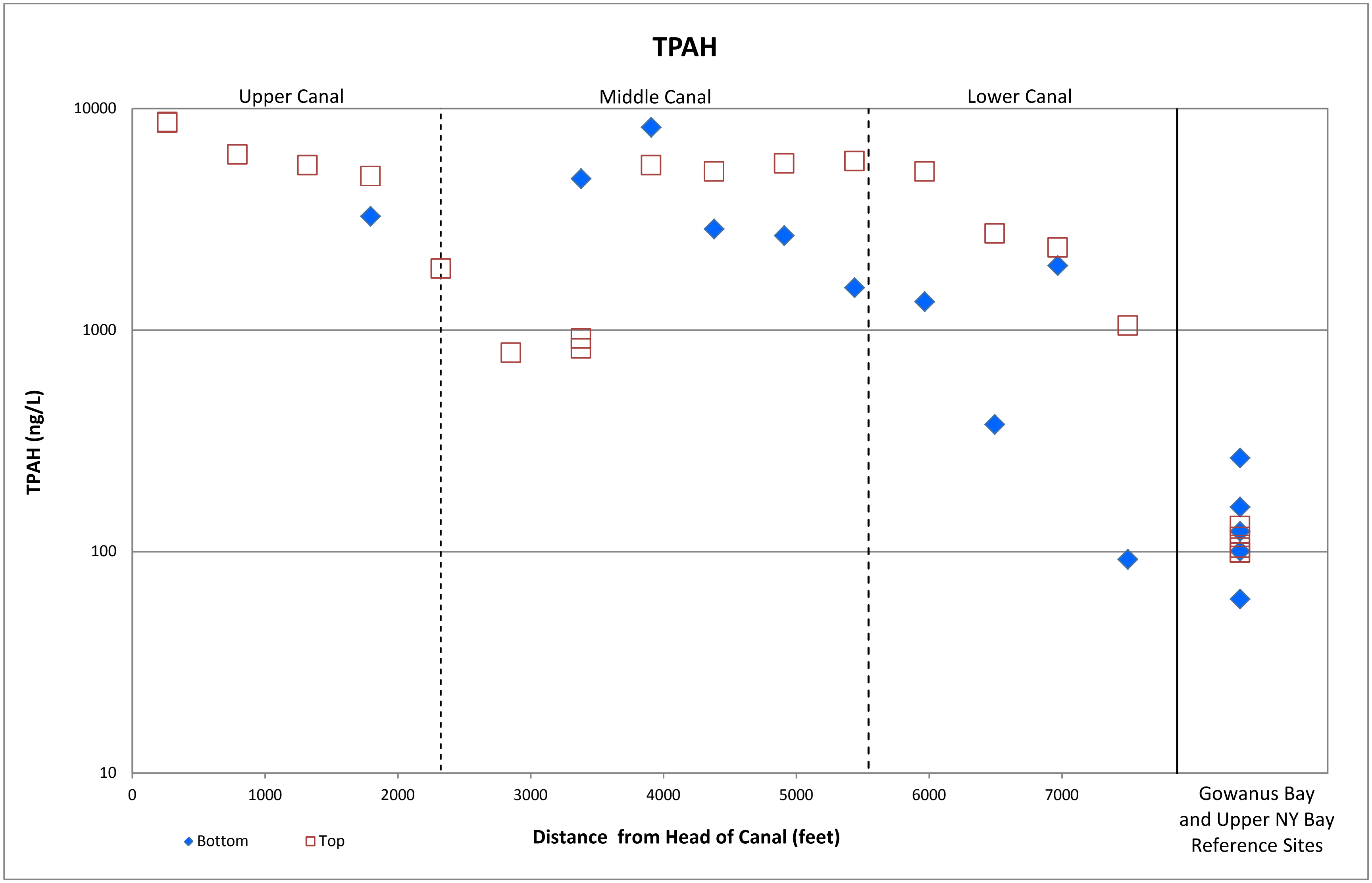


Water Column Whole Water Concentrations – Phenanthrene

Gowanus Canal Superfund Site

Figure A2.2-7

April 2013



Water Column Whole Water Concentrations – TPAH

Gowanus Canal Superfund Site

Figure A2.2-8

April 2013

Appendix A3 –Chemical Concentrations and Mass Balance in Gowanus Upper Canal

Table of Contents

A3. Chemical Concentrations and Mass Balance in Gowanus Upper Canal

Much of the contamination found within the Gowanus Canal is associated with the sediment that lines the canal bottom as well as contamination that enter from external sources and adjacent areas. Understanding the various contaminant inputs to the canal is critical to completing a conceptual site model (CSM) and is essential to determining the effectiveness of remedial strategies. For this reason, it is necessary to establish the importance of each potential source of contamination to the Gowanus Canal. A chemical mass balance approach is one of the tools used to understand the relative importance of the contaminant sources and their fate and transport in contaminated waterbodies.

This appendix provides a contaminant fate and transport analysis for the Upper Canal based on a chemical mass balance approach. The chemical mass balance was constructed using average concentrations to represent sediment inputs from CSOs and the reference area. The mass balance is presented as a sensitivity analysis consisting of several hypothetical scenarios of solids input from CSOs into the Upper Canal. The objective of the appendix is to evaluate the following questions:

- How do average chemical concentrations in CSOs compare to concentrations in the Upper canal and reference area?
- Is sediment transport correlated to contaminant transport in the Upper Canal?
- Is the FS Addendum hypothesis that CSOs constitute the majority of the contamination in the surface sediment valid?
- Is there evidence to support the existence and magnitude of other sources of contamination?

A3.1. Comparing Chemical Concentration in the Solids Sources Relative the Upper Canal

Geochemical evaluations were performed to characterize the chemicals in solids sources (CSOs and Gowanus Bay Reference Area), relative to the Upper Canal. The chemicals evaluated included: total organic carbon (TOC), metals, Total PAHs, acenaphthene, benzo(b)fluoranthene, benzo(k)fluoranthene, phenanthrene, pyrene, and Total PCBs. The following section describes the concentrations on a chemical by chemical basis. In each instance, the average concentration is the value used in the mass balance. For PCBs, multivariate analysis was performed to discern the difference in PCB congener patterns between the CSO solids, the Gowanus Bay reference area sediments and surface sediments in the Canal.

A3.1.1. Total Organic Carbon

Measured TOC content from the CSO solids, Upper Canal and Gowanus Bay reference area is shown in the left panel of **Figure A3-1a**. The TOC on CSO solids ranged from 27 to 50 percent, with an average of 40 percent. The TOC in the Upper Canal soft sediment ranged from 1.3 to 11 percent, with an average of 6 percent. The reference area TOC ranged from 0.3 to 5.4 percent, with an average of 3 percent. As can be seen in the figure, the TOC concentration for CSO solids is significantly higher than that of the Upper Canal sediment and reference areas sediment.

A3.1.2. Metals

Copper

Average copper concentration in the CSO solids is about two and six times higher than the Upper Canal sediment and the reference area concentration, respectively. The left hand panel of **Figure A3-1b** shows copper concentration in the CSO solids, Upper Canal and reference area. Copper concentration in the CSO solids ranged from 150 to 730 mg/kg, with an average of approximately 370 mg/kg. The Upper Canal copper concentration ranged from 66 to 150 mg/kg, with an average of approximately 200 mg/kg.

The reference area copper concentration ranged from 15 to 80 mg/kg, with an average concentration of approximately 70 mg/kg.

Lead

Unlike copper, the average lead concentration for the CSO solids is comparable to that of the Upper Canal. The average lead concentration in the CSO solids and Upper Canal is approximately 360 and 345 mg/kg, respectively. The reference area average lead concentration is about 5 times lower than that of the CSO solids and the Upper Canal (right panel of **Figure A3-1b**).

Cadmium

Figure A3-1c shows cadmium concentrations from the CSO solids, Upper Canal and reference area (left panel). Similar to lead, the average cadmium concentration for the CSO solids and the Upper Canal is comparable. The average cadmium concentration from the CSO solids and the Upper Canal is approximately 3 and 2.5 mg/kg, respectively. The average cadmium concentration from the reference area is about two times lower than that of the CSO solids and the reference area.

Chromium

Unlike the other metals listed above, the average chromium concentration in the Upper Canal is about two times higher than the concentration from the CSO solids. The average chromium concentration in the Upper Canal is about 1.2 times higher than that of the reference area. Right panel of **Figure A3-1c** shows the chromium concentrations from the three different sources. The chromium concentrations from the CSO solids ranged from 6 to 60 mg/kg, with an average concentration of 34 mg/kg. Chromium concentrations from the Upper Canal ranged from 23 to 110 mg/kg, with an average concentration of 63 mg/kg. In the reference area, chromium concentrations ranged from 17 to 66 mg/kg, with an average of 52 mg/kg.

Zinc

The average concentration of zinc on the CSO solids is about two times higher than that of the Upper Canal and about six times higher than that of the reference area (left panel of **Figure A3-1d**). The average concentration of zinc from the Upper Canal sediments is about three times higher than that of the reference area. The zinc concentrations on CSO solids ranged from 380 to 1,400 mg/kg, with an average concentration of approximately 880 mg/kg. In the Upper Canal, zinc concentrations ranged from 195 to 950 mg/kg, with an average concentration of approximately 460 mg/kg. In the reference area, zinc concentrations ranged from 63 to 250 mg/kg with an average concentration of 150 mg/kg.

A3.1.3. Total PCB Congeners

The Total PCB congeners' concentration on the Upper Canal sediments is about two times higher than the concentrations on both CSO solids and reference area sediments (right panel of **Figure A3-1d**). The Total PCB concentration in the CSO solids ranged from 240 to 940 mg/kg, with an average value of approximately 450 mg/kg. In the Upper Canal, the Total PCB concentrations ranged from 100 to 1,650 mg/kg, with an average value of approximately 700 mg/kg. The reference area Total PCB concentrations ranged from 220 to 670 mg/kg, with an average value of approximately 420 mg/kg.

Because PCBs are persistent compounds that are also highly particle reactive, PCB mixtures in the environment largely retain the patterns of the sources responsible for them. The City prepared a principal components analysis (PCA) to examine the patterns of PCBs in the sediments of the Canal as well as in the known solids sources. The reader is referred to a standard statistical text for a complete definition of PCA procedures and their application. For the purposes here, PCA is basically a statistical basis to enable the analyst to group samples of similar pattern and identify various groups of samples that have similar patterns. In applying a PCA to sediments and solids, it often possible to distinguish various PCB sources to the environment.

In this analysis, suspended solids data from the CSOs by the City, surface sediment data obtained by the City and surface sediment data obtained by EPA were included in the data set. In all instances, congener-specific analyses are required since the large number of PCB congeners provides a robust basis to identify PCB patterns. These data were reviewed to identify the PCB congeners that occurred most frequently and that comprised the greatest amount of the PCB mass in the sample. Based on this review, 118 PCB congeners were included in the PCA, representing 95 percent or more of the total PCB mass in the sample.

The PCA analysis is most useful when it is applied to identify differences in PCB pattern and not in absolute concentration. In examining environmental patterns, it is most useful to know if the PCB pattern has changed, indicating another source of PCBs, and not whether the absolute PCB concentration has changed. Absolute changes in concentration can occur in response to variations in the fine-grained fraction, since this fraction carries the vast bulk of the PCB mass. Thus, variations in this fraction will cause variations in absolute PCB concentration, but no change in PCB pattern.

To avoid concerns with absolute concentration, the 118 PCB congeners were then normalized by the sum of 118 PCB congeners to create a mass fraction for each congener in each sample. The 118 PCB congeners mass fractions were imported into the software JMP[1] and a PCA were then generated. Figure **A3-1e** shows a scatter plot of the data against the two primary principal components determined from the analysis. The samples are plotted on the diagram with different symbols for the different sampling programs and color-coded by the various concentration ranges. The first principal component (PC1) explains 46 percent of the variance in the data and PC2 represents about 16 percent of the variance in the data. **Figure A3-1e** shows the results of the analysis for the CSO and sediment samples. Also added to the diagram are points representing Aroclors 1242, 1248, 1254 and 1260 patterns, based on the congener work by Frame *et al.*, 1996. These points represent patterns of PCB congeners that were commonly used and often discharged in industrial wastewater.

As a result of the PCA, the data splay into a triangular area on the diagram. Nearly all sediment samples fall along a line connecting Aroclor 1248 and Aroclor 1260, suggesting these mixtures are characteristic of the source materials to the sediments. Of particular note are the high concentrations in the sediment as indicated by color, which fall closest to the Aroclor-1260 pattern, indicating that the most concentrated source of PCBs to the surface sediments of the Canal is Aroclor 1260-like. Essentially this line of sediment samples suggests a mixing system involving relatively low level harbor solids and a source of more highly concentrated PCBs to the Canal. This source is clearly not CSO-related, however. The CSO solids tend toward an Aroclor 1254-like member and there are few if any sediment samples with similar patterns. Additionally, these CSO solids are low in PCB concentration and thus cannot be the source of the sediments that are ten to thirty times more contaminated, found on the bottom of the Canal. **Figure A3-1f** shows the results for sediments alone, with a line characterizing the mixing regime between harbor solids and the most contaminated sediment sample available for this analysis. From the diagram, it is clear that are no sediment samples that are strongly impacted by the CSO PCB patterns, and by inference, CSO PCB contributions.

A3.1.4. PAHs

The concentration of Total PAHs, acenaphthene, benzo(b)fluoranthene, benzo(k)fluoranthene, phenanthrene and pyrene are all examined in this section. All the PAHs examined showed similar relationships among the three solids types, in which the average concentration in the Upper Canal sediment is higher than the average concentrations on both the CSO solids and the reference area sediments (**Figures A3-1g through A3-1i**). The average PAH concentration for the Upper Canal sediment is about 4 to 38 times higher than that of the CSO solids, depending on the individual PAH

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[1] JMP is a statistical software developed by SAS Institute, Inc. http://www.jmp.com/

compound. Compared to the reference area average PAH concentration, the Upper Canal average sediment PAHs concentration is about 8 to 100 times higher. The CSO solids average PAH concentration is about 2 to 4 times higher than that of the reference area sediment concentration.

A3.2. Chemical Mass Balance in the Gowanus Upper Canal

A chemical mass balance was calculated for the sediments of the Upper Canal. The mass balance was calculated by using two known sources of solids to the Canal, the CSO solids and the Gowanus Bay reference area sediment.

Each of the main COPCs listed in the FS addendum are included in the mass balance analysis, including: copper lead, Total PAHs and Total PCBs. However, TOC, additional metals and individual PAHs were added to the mass balance to including: cadmium, chromium and zinc, acenaphthene, benzo(b)fluoranthene, benzo(k)fluoranthene, phenanthrene and pyrene. These metals and PAHs were added because they provide additional constraints on the mass balance analysis and provide additional information to evaluate the FS addendum hypothesis on the main source of solids and contaminants to the Upper Canal.

The chemical mass balance model is set up as a linear mixing process between solids contributed by the CSOs and the solids originating from the harbor (*i.e.*, the reference area sediment). The model assumes that the chemical burden on the solids from these two inputs is the only chemical contribution to the Upper Canal. Based on this approach, the current average surface sediment concentrations in the Upper Canal can be represented with the following chemical mass balance equation:

$$C_{uc} = \frac{C_{cso} \times S_{cso}}{C_{ra} \times S_{ra}} \qquad \text{Equation 1}$$

where

C_{uc} = chemical concentration normalized to aluminum in the Upper Canal surface sediment
C_{cso} = chemical concentration normalized to aluminum in CSO solids
S_{cso} = solids fraction from CSOs
C_{ra} = chemical concentration normalized to aluminum in the reference area
S_{ra} = $1 - S_{cso}$ = solids fraction from the reference area

When Equation 1 was applied for each chemical, the solids contributors were represented by their chemical concentration normalized to aluminum. Aluminum was selected as a normalizer to account for differences in particle composition in the system. Absolute changes in concentration can occur in response to variations in the fine-grained fraction of sediment, since this fraction carries the vast bulk of surface–bound contaminants, such as the ones involved in this analysis. Thus, variations in this fraction will cause variations in absolute concentration, but no change in contaminant patterns. By normalizing to aluminum, which is largely associated with the fine-grained fraction, the mass balance analysis focuses on the contributors to the fine-grained fraction of the sediments, where the contaminants are stored.

The model simulations were performed as follows:

- Determined the average aluminum normalized chemical concentrations for the CSO solids, the Gowanus Bay reference area sediments and the Upper Canal surface sediments.
- Assumed a hypothetical solids contribution from the CSOs. Five hypothetical scenarios of CSO solids contributions were included: 10 percent, 30 percent, 50 percent, 70 percent and 90 percent.
- Applied Equation 1 for each chemical and each hypothetical solids contribution from the CSOs. Determined the model predicted aluminum normalized surface sediment concentrations.
- Compared the model results with the actual normalized sediment concentrations in the Upper Canal. Calculated the percent deviation, defined in Equation 2 below. Note that a positive

deviation indicates that the inputs to the Canal are greater than required to yield the observed Upper Canal normalized surface sediment concentration, while a negative deviation indicates that significant additional sources are needed to yield the observed normalized surface sediment concentration in the Upper Canal.

$$\%Deviation = \frac{C_{cu} - C_{a\_cu}}{C_{a\_cu}} \times 100\% \qquad \text{Equation 2}$$

where

$\%Deviation$ = Percent deviation of the calculated chemical concentration
C_{uc} = calculated chemical concentration in the Upper Canal surface sediment
C_{a_cu} = actual chemical concentration in the Upper Canal surface sediment

Results of percent deviation for the various hypothetical CSO solids scenarios are given in **Figure A3-2**. The results from the mass balance analysis for the various solids scenarios are presented below.

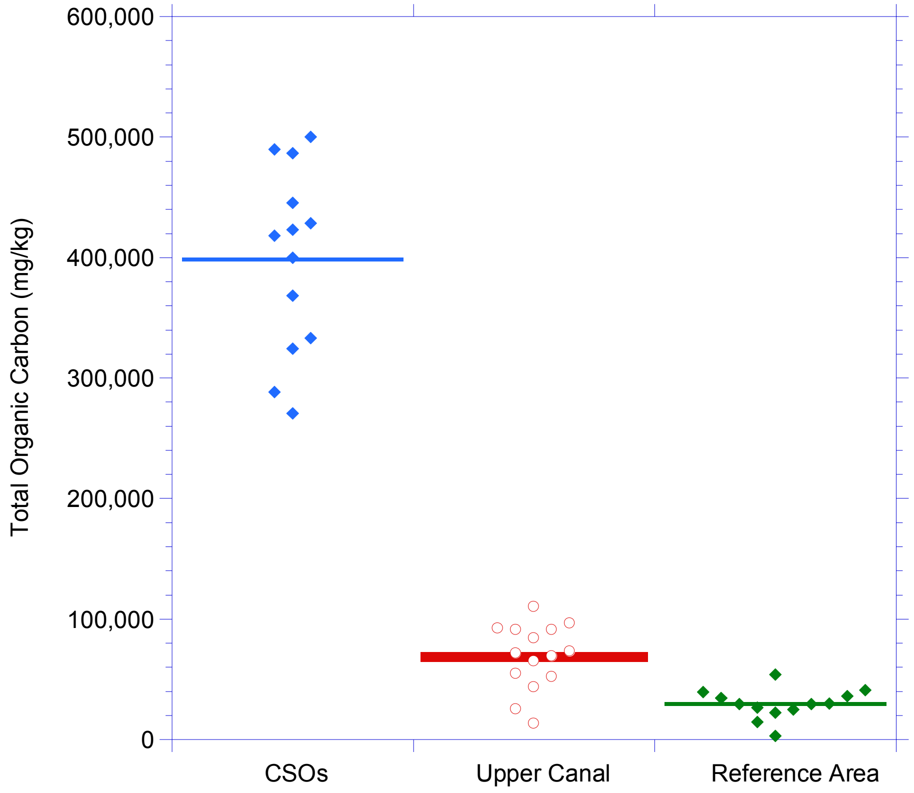
- For the hypothetical scenario of a 10 percent CSO solids contribution, the simulated Upper Canal surface sediment normalized concentration is under predicted for all chemicals except TOC, resulting in large negative percent deviations (**Figure A3-2a**).
- For the hypothetical scenario of 30 percent CSO solids contribution, the simulated normalized copper concentration is within 4 percent of the normalized observed surface sediment concentration in the Upper Canal. TOC is over predicted by 55 percent. Lead and zinc are under predicted by about 50 percent and 20 percent, respectively. TPCB is under predicted by 20 percent. PAHs are under predicted by 70 percent or more (**Figure A3-2b**).
- For the hypothetical scenario of 50 percent CSO solids contribution, only cadmium is simulated to within 2 percent of the normalized observed surface sediment concentration in the Upper Canal. Copper goes from a close match to being over predicted while zinc switches from being under predicted in the previous scenarios to being over predicted, meaning that we have more inputs of these metals than required. Lead and PCBs continue to be under predicted by 30 percent and 10 percent, respectively. PAHs remain under predicted by 70 percent or more (**Figure A3-2c**).
- For the hypothetical scenario of 70 percent CSO solids contribution, TOC, copper, cadmium and zinc are all over predicted, while lead and chromium are under predicted. Predicted TPCB is now within 2 percent of the observed average surface sediment normalized concentrations. Lead is simulated to within 2 percent of the normalized observed surface sediment concentration in the Upper Canal. Copper and zinc switch from being under predicted in the previous scenarios to being over predicted, meaning that we have more inputs than required. Lead and PCBs continue to be under predicted by 30 percent and 10 percent, respectively. PAHs are under predicted by 60 percent or more (**Figure A3-2d**).
- For the hypothetical scenario of 90 percent CSO solids contribution, copper and zinc are over predicted by more than 100 percent. Lead changes from being under predicted in previous scenarios to being over predicted by 10 percent. TPCB is over predicted by 10 percent. PAHs are under predicted by 50 percent or more (**Figure A3-2e**).

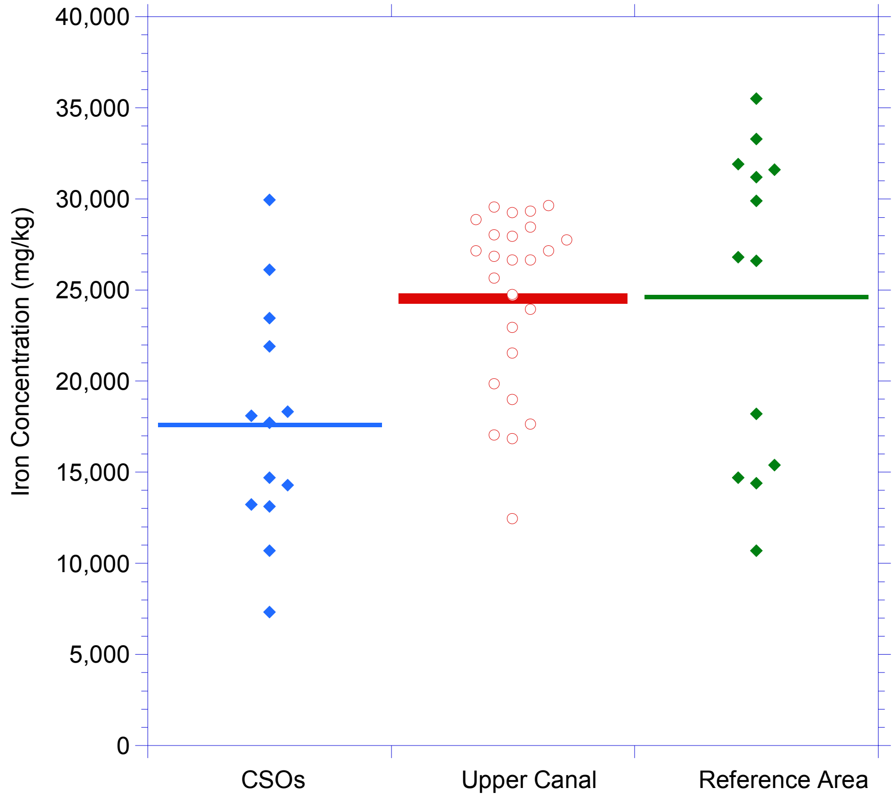
The results of the chemical mass balance highlight several important observations as follows:

- There is no combination of CSO solids and Gowanus Bay sediment that can simultaneously explain the surface sediment concentrations in the Upper Canal for all the chemicals.
- Because there are no combinations of solids that can explain the contamination in the Upper canal, solids transport is not correlated to contaminant transport. There are significant sources of contamination to the canal that are not associated with solids transport, for example, groundwater.
- Given the large deviation between the chemical mass balance prediction and the observed Upper Canal surface sediment concentration for the 90 percent hypothetical CSO solids scenario, the FS addendum’s hypothesis that CSOs constitute the majority of the contamination in the surface sediment is not valid.

A3.3. Summary

The observations outlined by the City above, while disproving EPA's assertions on CSO contribution, provide an indication of how uncertainties in source characterization undermine the CSM and mass balance for the system. The fact that the chemical mass balance model for the Upper Canal cannot simultaneously explain all the chemicals evaluated suggests that large uncertainties exist with regard to the sources of contamination to the Canal. More importantly, it indicates that there is no correlation between sediment inputs and contaminant burden in the Canal. Therefore, any attempt to allocate responsibility for contamination in the Canal based on solids contribution will be incorrect. Given the unknown nature of these large contaminant loads, it is unclear that the current assemblage of upland investigation and remediation efforts will be able to control them all.





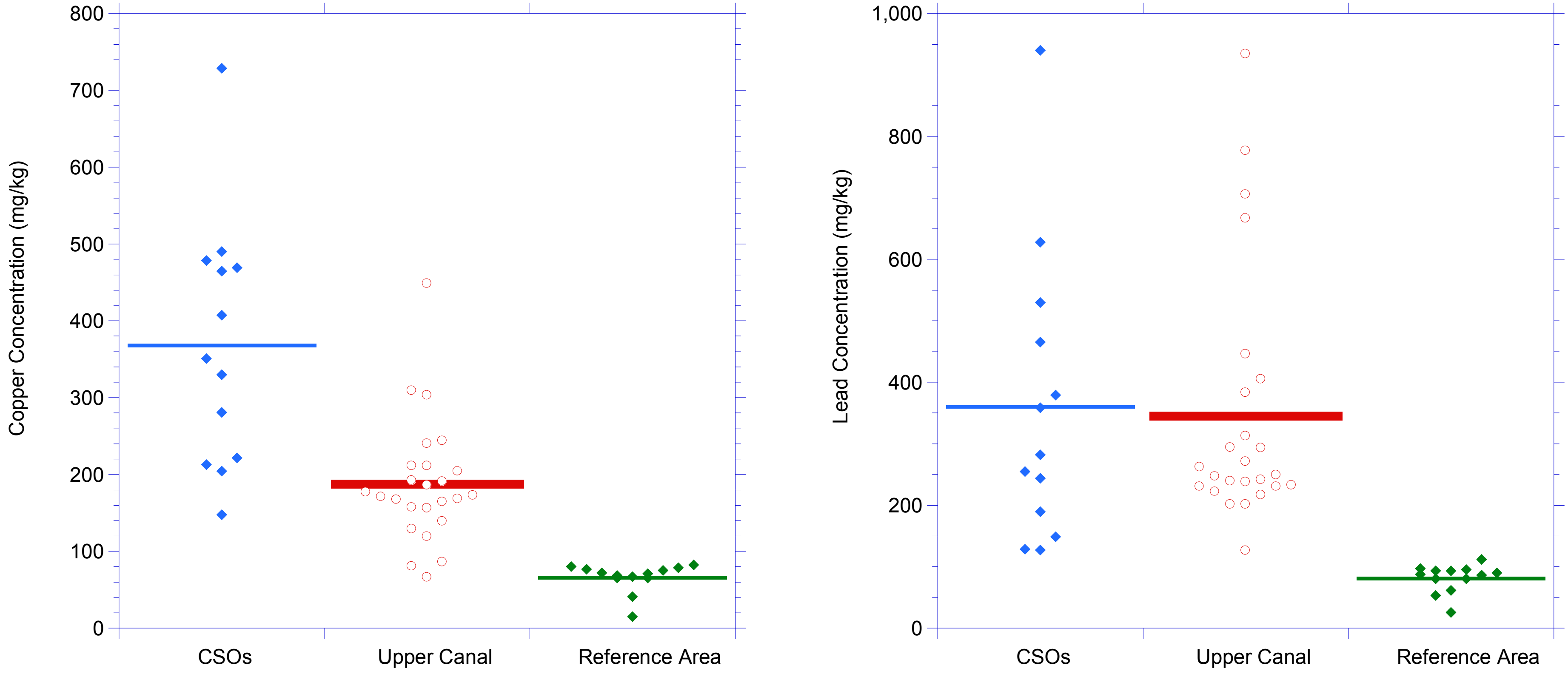
Environmental Protection

Total Organic Carbon and Iron Concentrations
CSOs, Upper Canal and Reference Area

Gowanus Canal Superfund Site

Figure A3-1a

April 2013

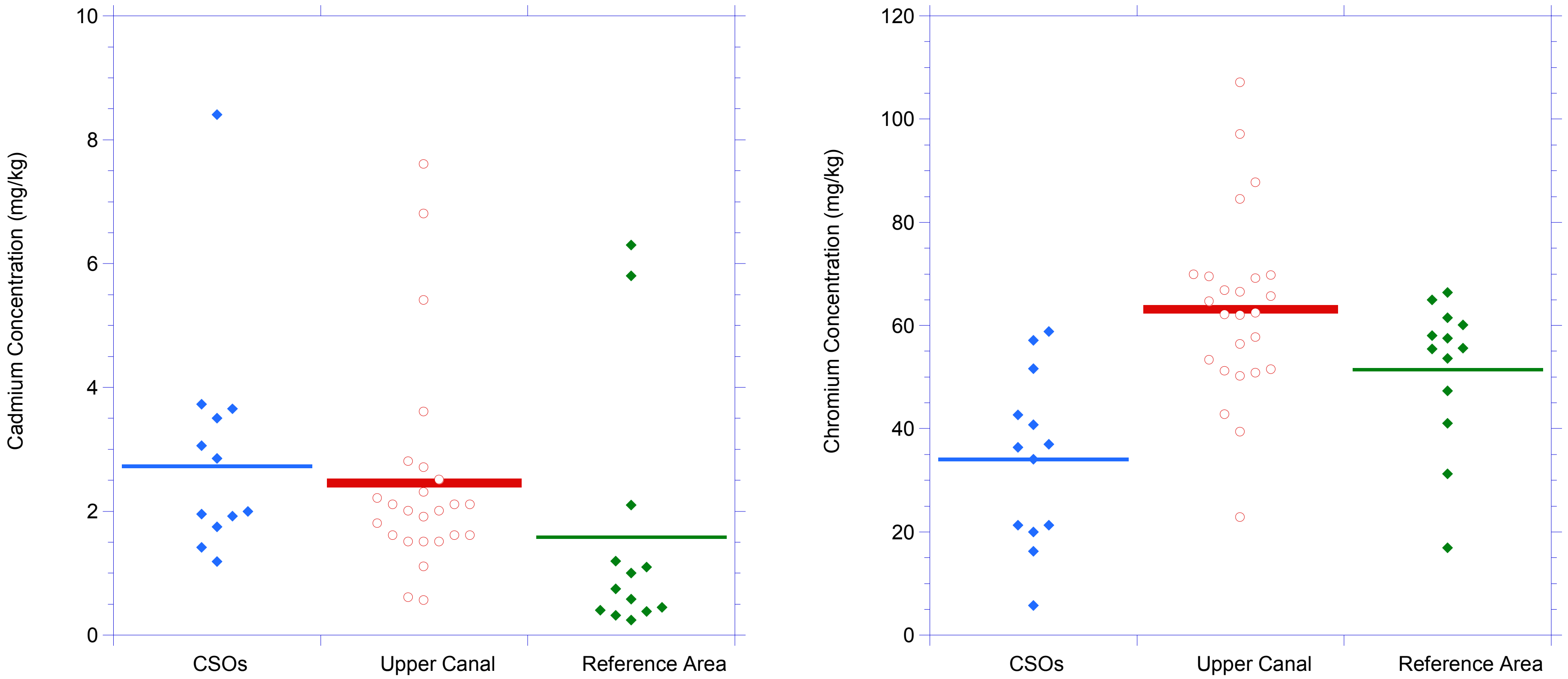


Environmental Protection

Copper and Lead Concentrations
CSOs, Upper Canal and Reference Area
Gowanus Canal Superfund Site

Figure A3-1b

April 2013



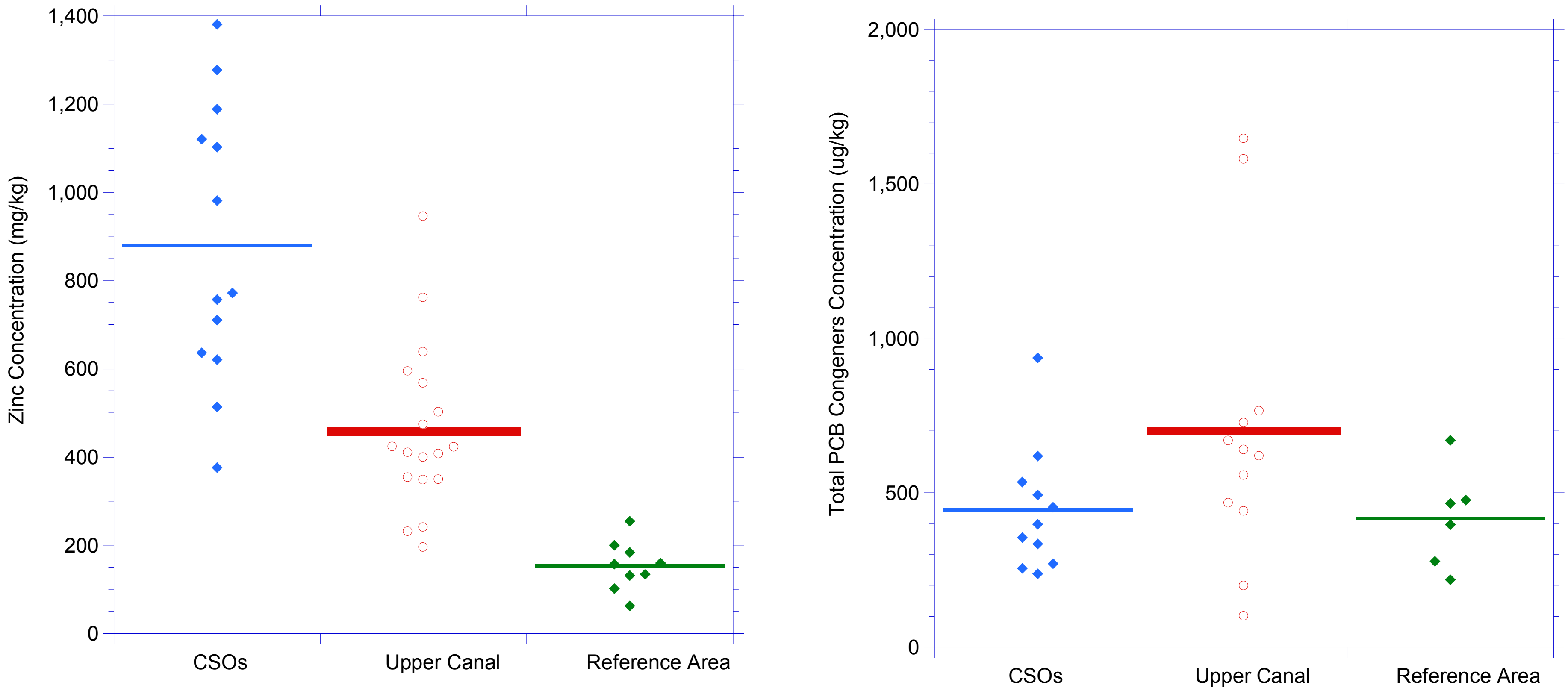
Environmental Protection

Cadmium and Chromium Concentrations
CSOs, Upper Canal and Reference Area

Gowanus Canal Superfund Site

Figure A3-1c

April 2013



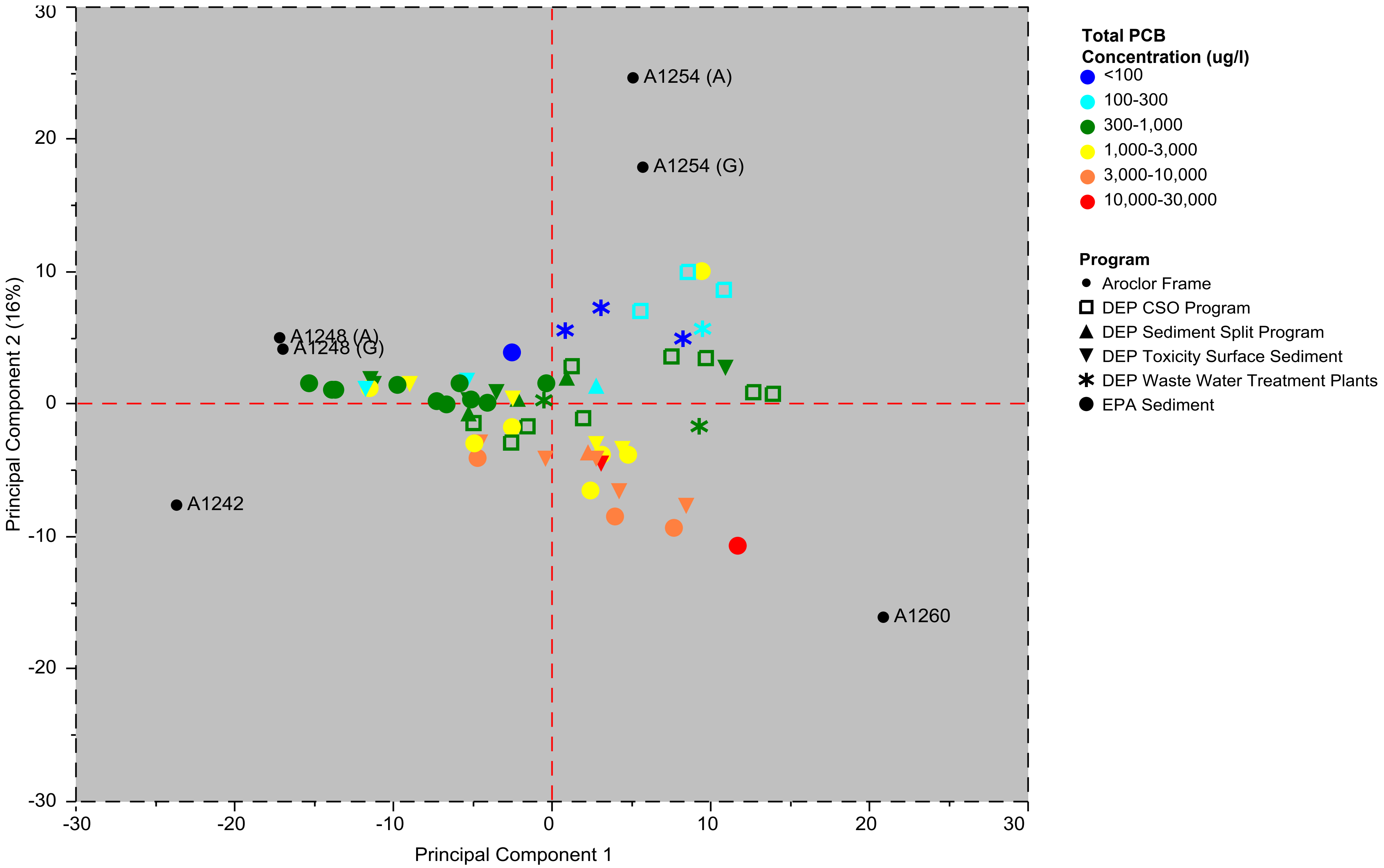
Zinc and Total PCBs Concentrations

CSOs, Upper Canal and Reference Area

Gowanus Canal Superfund Site

Figure A3-1d

April 2013



Note:
(A) Or (G) indicate aroclor lot number. (A) was from AccStandard, New Haven, CT, USA. (G) was from Monsanto Corp., St. Louis, MO, USA.

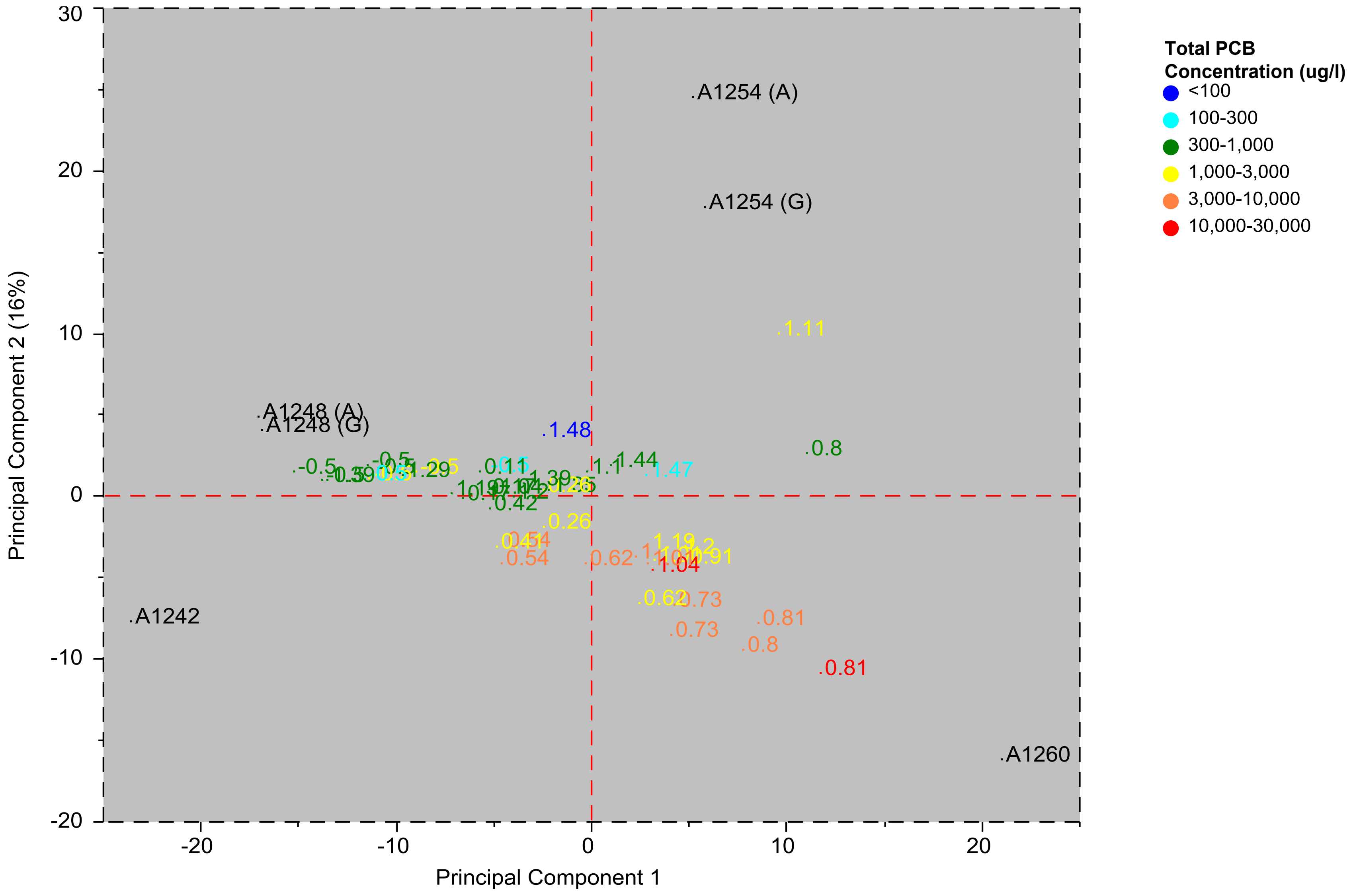
Environmental Protection

CSOs and Surface Sediments Principal Component Analysis

Gowanus Canal Superfund Site

Figure A3-1e

April 2013



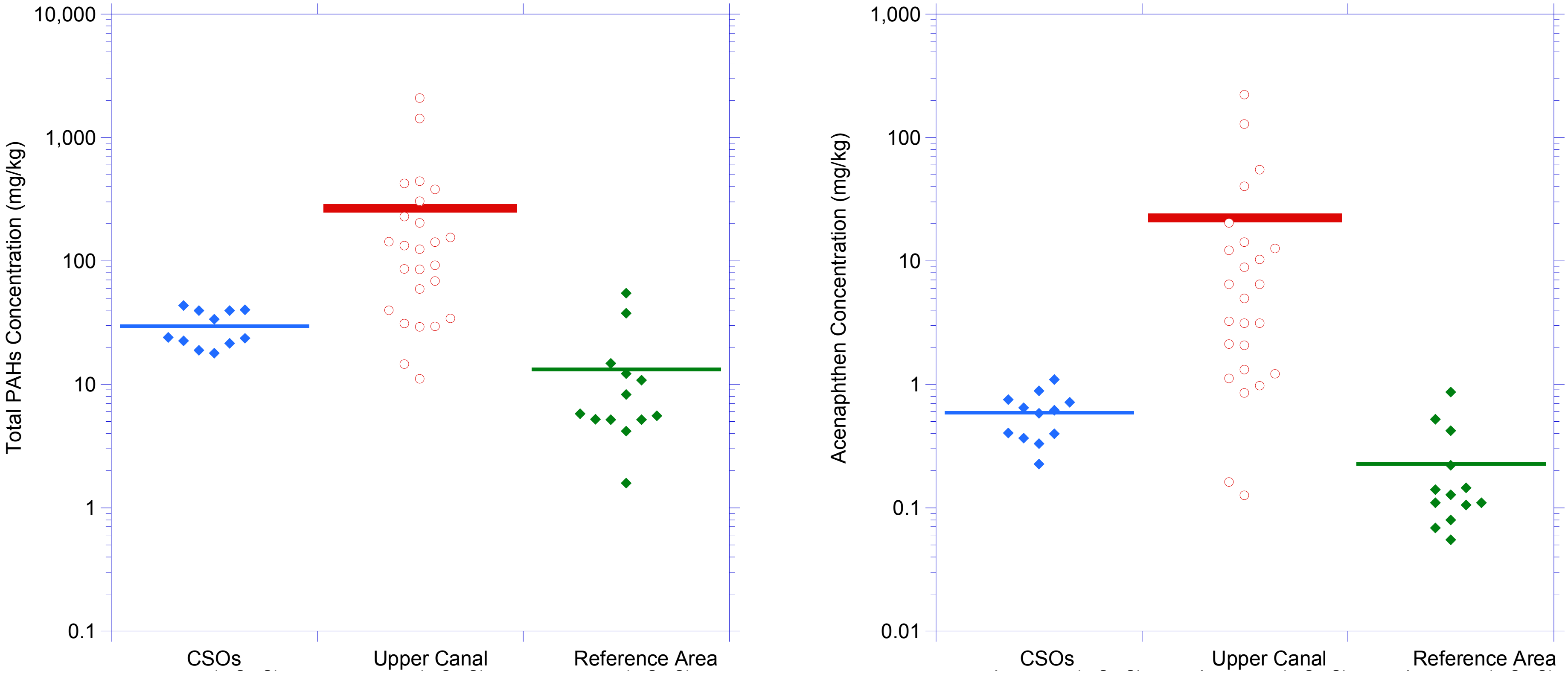
PCB Congeners PCA Results

Sediment Data

Gowanus Canal Superfund Site

Figure A3-1f

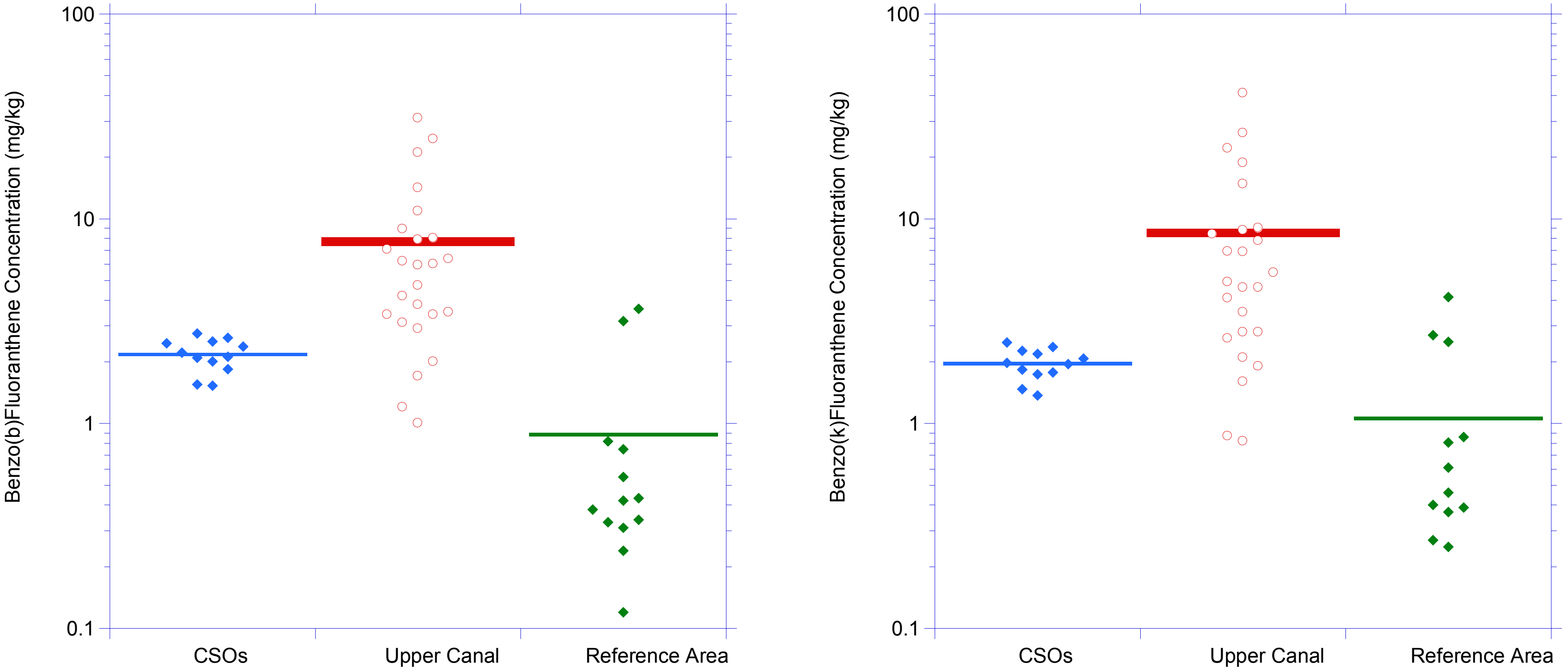
April 2013



Total PAHs and Acenaphthene Concentrations
CSOs, Upper Canal and Reference Area
Gowanus Canal Superfund Site

Figure A3-1g

April 2013

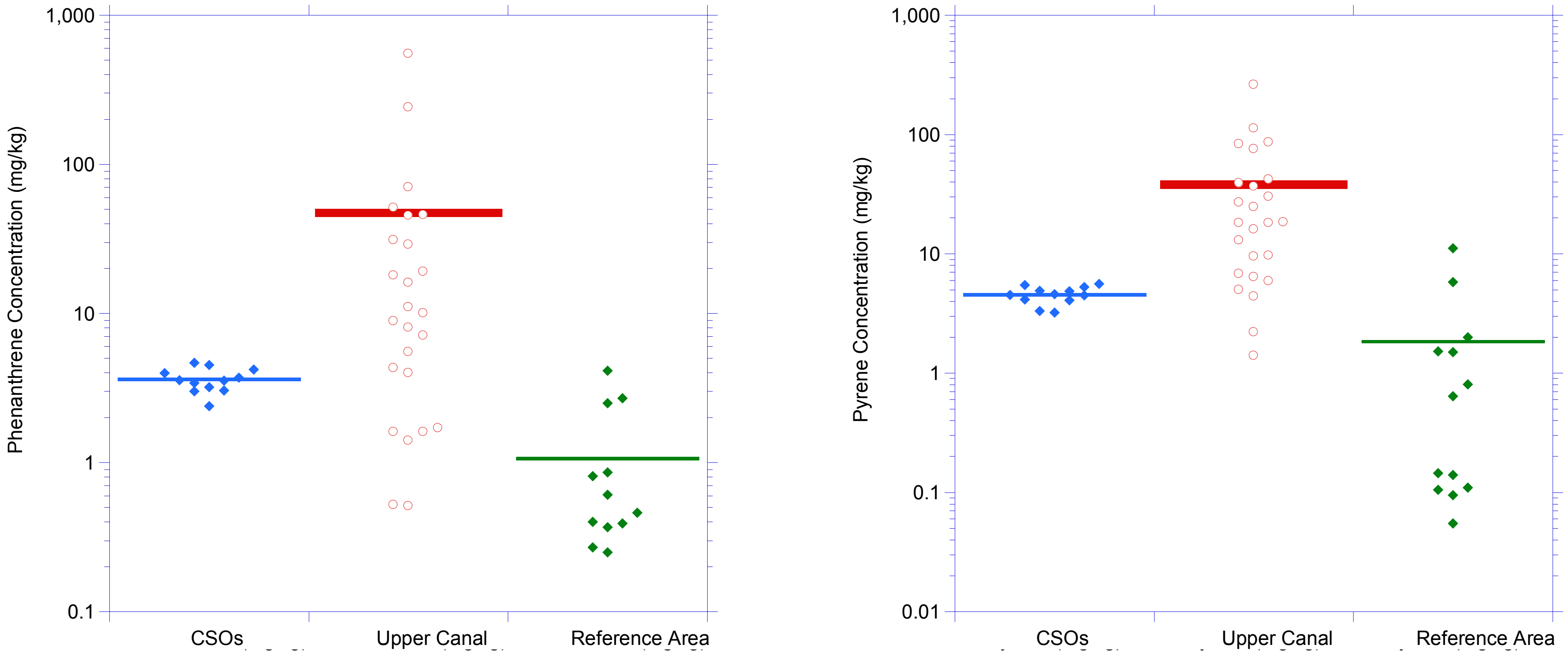


Benzo(b)Fluoranthene and Benzo(k)Fluoranthene Concentrations
CSOs, Upper Canal and Reference Area

Gowanus Canal Superfund Site

Figure A3-1h

April 2013

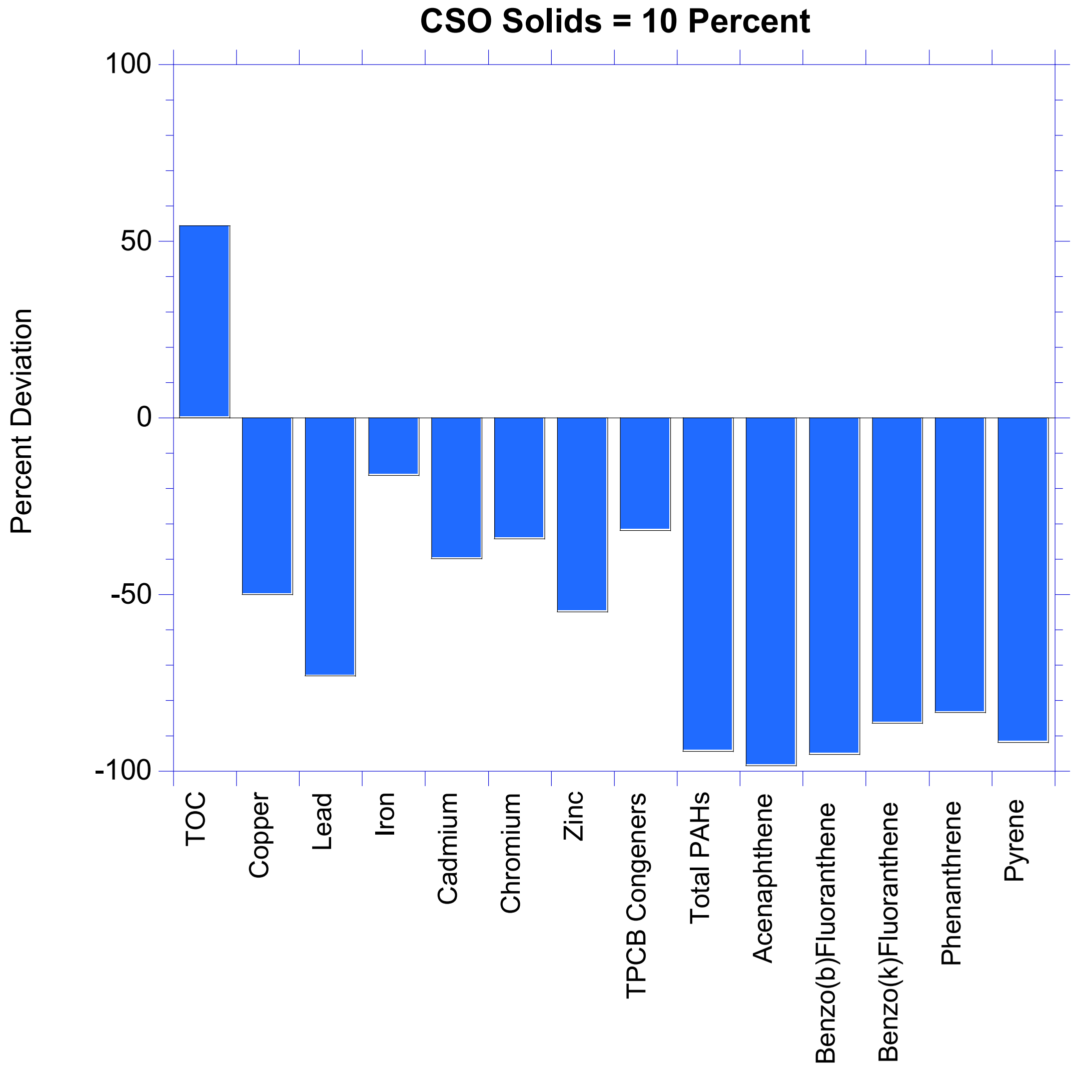


Environmental Protection

Phenanthrene and Pyrene Concentrations
CSOs, Upper Canal and Reference Area
Gowanus Canal Superfund Site

Figure A3-1i

April 2013



Excess Loads

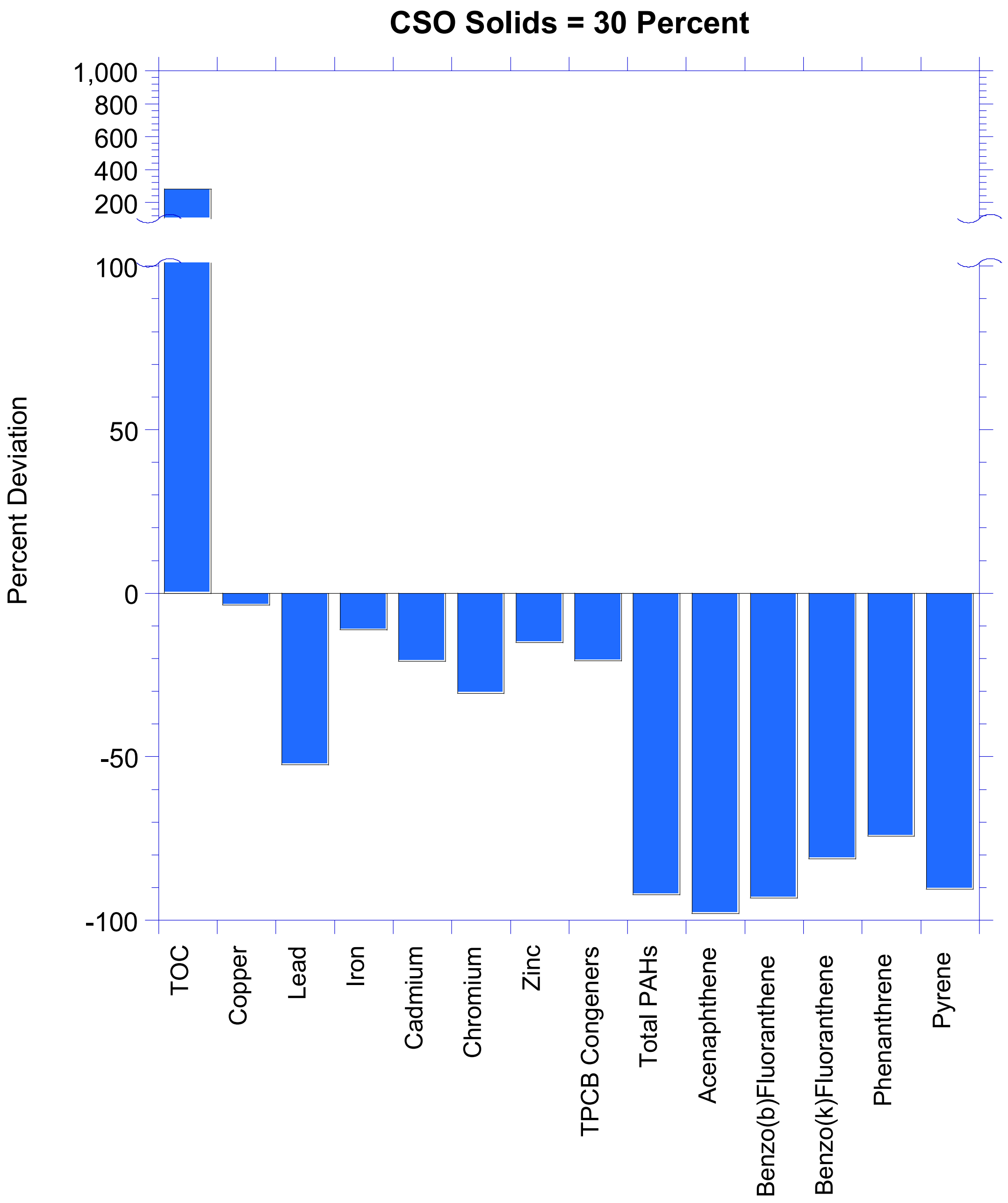
Insufficient Loads

Chemical Mass Balance Model Performance for 10% CSO Solids Contribution
Hypothetical Scenario

Gowanus Canal Superfund Site

Figure A3-2a

April 2013



Excess Loads

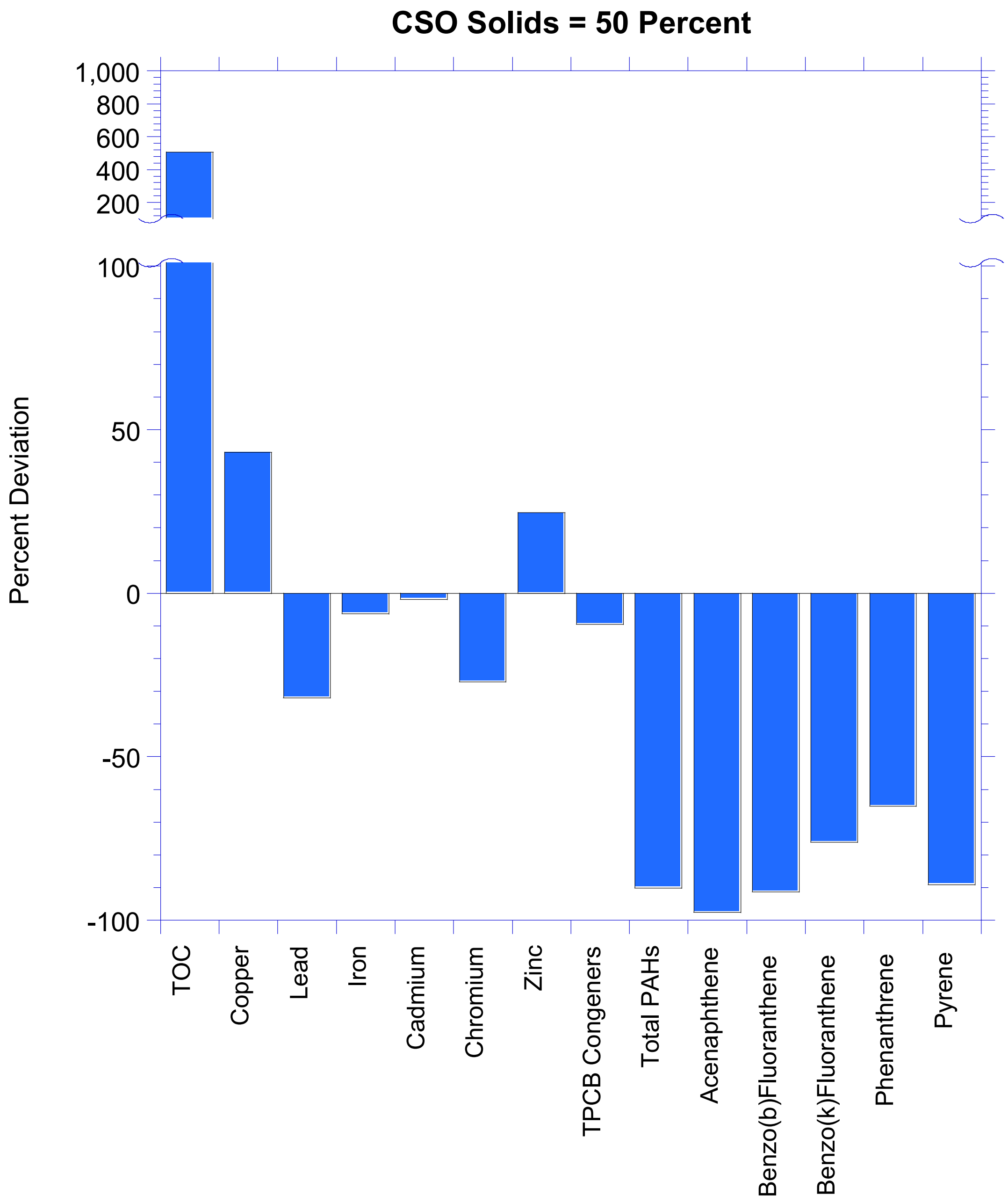
Insufficient Loads

Chemical Mass Balance Model Performance for 30% CSO Solids Contribution
Hypothetical Scenario

Gowanus Canal Superfund Site

Figure A3-2b

April 2013



Excess Loads

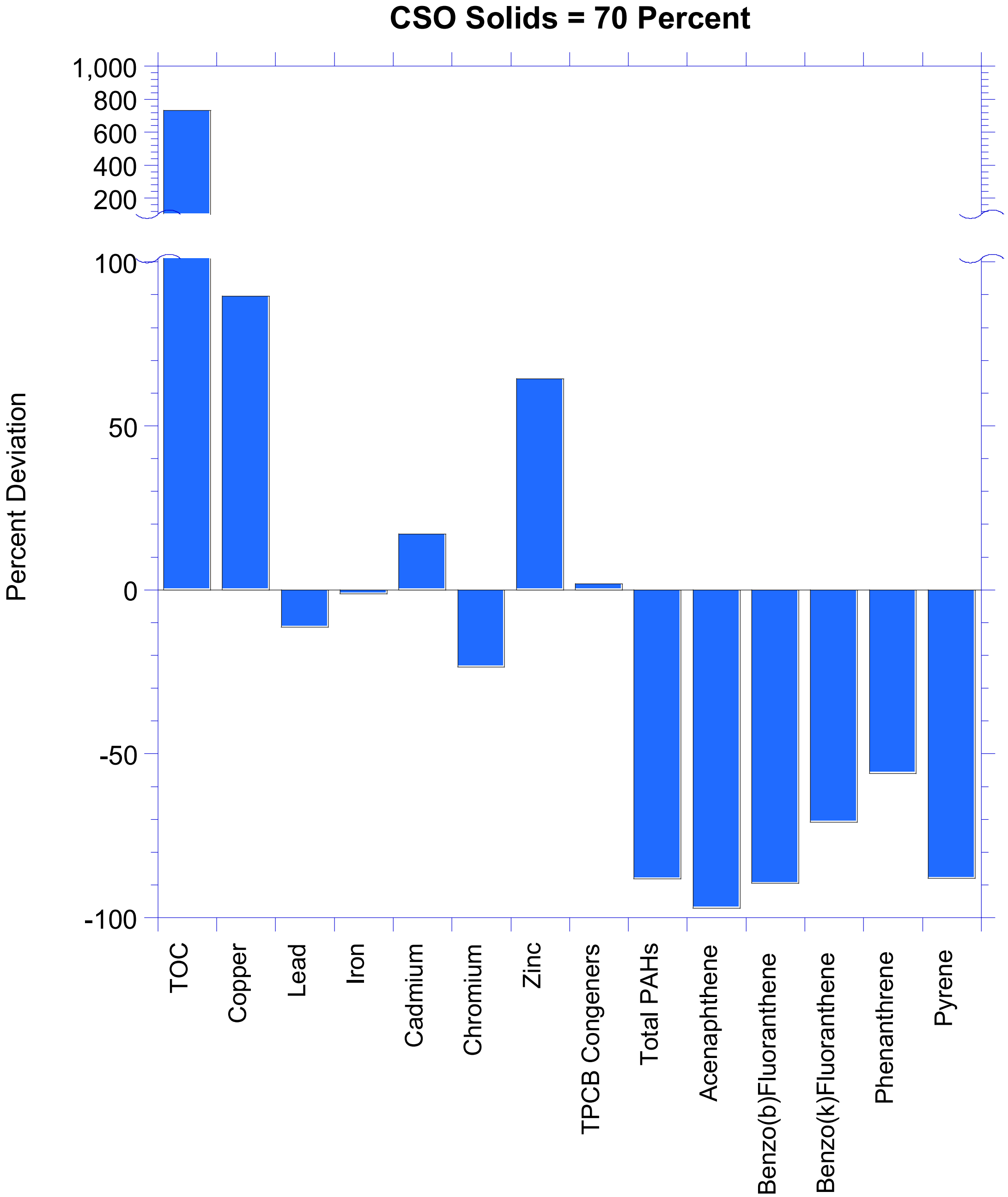
Insufficient Loads

Chemical Mass Balance Model Performance for 50% CSO Solids Contribution
Hypothetical Scenario

Gowanus Canal Superfund Site

Figure A3-2c

April 2013



Excess Loads

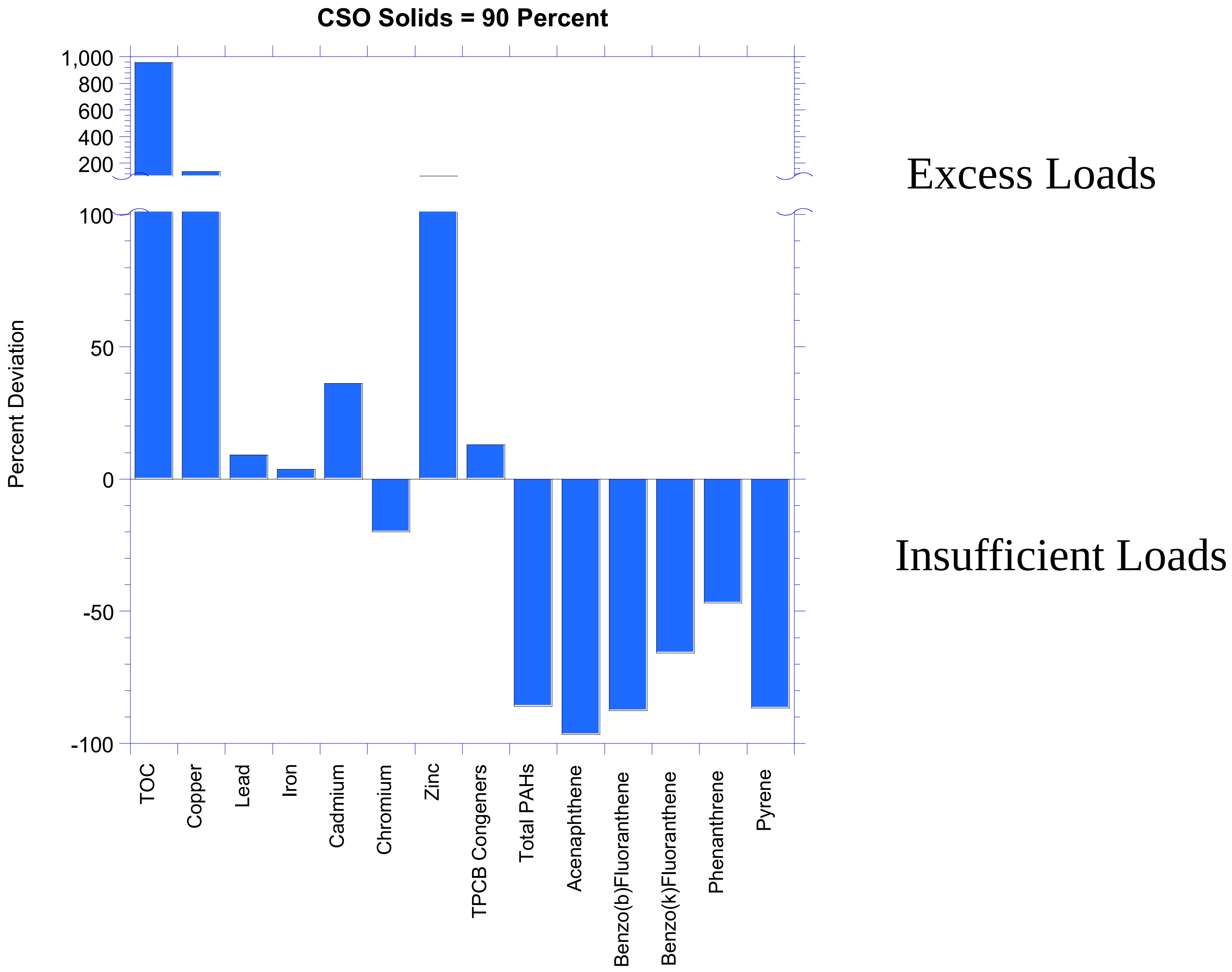
Insufficient Loads

Chemical Mass Balance Model Performance for 70% CSO Solids Contribution
Hypothetical Scenario

Gowanus Canal Superfund Site

Figure A3-2d

April 2013



Chemical Mass Balance Model Performance for 90% CSO Solids Contribution
Hypothetical Scenario

Gowanus Canal Superfund Site

Figure A3-2e

April 2013

Appendix A4 – Risk Assessment

Table of Contents

A4. Risk Assessment

A4-1. Technical Basis for Reference Envelope Approach

A4-1.1. Introduction

The Reference Envelope statistical approach is used to characterize differences between potentially contaminated sites and regional areas unaffected by contaminants of concern. The approach can be used with sediment toxicity testing to characterize a contaminated site and compare it with regional reference areas that are not affected by the contaminant(s) of concern.

The objective of reference envelope approach is different from determining absolute sample toxicity. Rather than comparing the results of test samples with laboratory controls using laboratory replicate variance as the statistical test variance component, the reference envelope method establishes *tolerance limits* based on test results from reference area samples (*i.e.*, the comparison is between contaminated sites and regional reference areas, rather than contaminated sites vs. laboratory control samples).

The strength of the reference envelope method lies in the ability to account for a number of relevant sources of variation that could affect comparisons between the site and the reference areas, such as variation in sampling time and space, or variation between replicates in a toxicity test. Mean test responses for the reference sites are assumed to represent the normal range of responses of organisms to sediments from the study area in the absence of contamination. Therefore, if natural factors such as grain size vary among reference sites or between surveys, these factors are accounted for in the results. Any additional change in the test response (*i.e.*, increased toxicity) is assumed to be attributable to the increased pollution at the test site(s).

A4-1.2. Technical Approach: Development of Tolerance Limits for Determining Toxicity

In the reference envelope approach, *Tolerance limits* are calculated to identify samples significantly more toxic than a chosen proportion of the reference site distribution, and statistical significance is determined using variation among reference site results (*i.e.*, the range of responses among reference area samples is quantified, and then the site sample results are compared to a *tolerance limit* or response derived from the range of reference area samples).

In calculating the tolerance limit, we would ideally like to know the exact toxicity at, for instance, the tenth percentile (*e.g.*, 90 percent of reference samples are less toxic). But we cannot know this exact percentile because we only have a number of *samples* from the underlying distribution. Therefore we need to estimate where the 10th percentile is. Note that the term *quantile* rather than *percentile* is often used in the context of tolerance limits. The percentile is equal to 100 times the quantile.

For any given project, the quantile (or percentile, "*p*") and the size of the confidence interval ("a") of that quantile must be chosen. For example the size of the confidence interval as a percentage could be 100(1-*a*) or 95 percent. If *a*=.05 and *p*=0.1 (lowest 10th percentile) were chosen we would assume that the computed tolerance interval estimate covered the actual 0.1 quantile of the underlying reference distribution with probability 1-.05. So, any test site sample with mean survival less than the tolerance limit would be assumed with 1-.05 percent (95 percent) confidence to be as toxic, or more toxic than the worst 10 percent of reference samples. **Figure A4.1-1** (from Hunt et al. 1998) illustrates the concept of the tolerance limit.

Next, it is necessary to compute the toxicity level that will cover the p^{th} percentile 1-a percent of the time as the Lower bound of the tolerance level (L).

$$\mathbf{L = Xr - [g_{a,p,n} * S_r]}$$

where

Xr is the mean toxicity result from the reference sample results;
$\mathbf{S_r}$ is the standard deviation of the toxicity results among reference area stations;
a is the accepted error probability associated with the estimate of the p^{th} percentile (.05 in the case above);
p is the percentile of interest (10 percent in the case above);
n is the number of reference stations;
g is a factor that varies depending on the experimental design and values chosen for *p* and *a*. These values can be obtained from Haan and Meeker (1991) or Gilbert (1987).

Only the lower tolerance limit is used when identifying samples with lower test results (i.e. lower survival) than expected of reference area samples.

- Note that this model assumes there is a single source of variance. In many studies there are more sources of error, including variance due to time (sampling event), space (sampling station), time by space interaction, and error (within time-space variance between replicates). If there is more than one source of error then a bootstrapping technique is required to derive an estimate for $\mathbf{g}_{a,p,n}$.

Examples

California Water Boards/Hunt et al. (1998, 2001), Ingersoll et al (2009), and MacDonald et al. 2009

Several studies have used the reference envelope approach. Two of interest, include the California Water Boards and associated scientists evaluation of sediment toxicity in San Francisco Bay (Hunt et al. 1998, 2001), and Ingersoll et al (2009) evaluation of sediments in the Ashtabula River in Ohio (Ingersoll et al. 2009).

Hunt et al. (1998, 2001) used the reference envelope approach to develop sediment toxicity standards against which to compare results from sites investigated in San Francisco Bay. The 1998 study included a thorough statistical analysis, including development of tolerance limits using three methods:

1) the simplest method computationally, based on “naïve variability” (assuming a single source of variance),
2) a method using bootstrap simulations to account for multiple sources of variation including sampling times and locations, and
3) a method that uses non-parametric methods to account for non-normally distributed data.

In these studies the calculated tolerance limits varied substantially with the selected quantile (*p*), treatment of outliers (whether outliers were removed or not), and the mean, variance, and number of data points in the reference site distribution. This shows the importance of both:

4) careful planning for field sampling to provide an adequate data set that can be used with this type of analysis, and
5) thorough documentation of all data analysis, including any removal of outliers.

Ingersoll et al. (2009) used the reference envelope approach to evaluate toxicity of contaminated sediments from the Ashtabula River in Northeastern Ohio to the amphipod *Hyalella Azteca*. In this study, data from a number of candidate reference areas was reviewed, and a subset was identified as appropriate for use as reference sediments based on sediment chemistry (average probable effect concentrations quotients [PEC-Qs] <0.2). Toxicity was established by comparing the test response (survival or length of amphipods) in site sediments to the response of amphipods exposed to reference sediments. Site sediment samples were designated as toxic if survival or length of amphipods in the sediments was lower than the lower limit of the normal range of responses for the reference sediments, with the lower limit of responses defined as the fifth percentile response of organisms exposed to reference sediments.

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Hunt, J.W., B.S. Anderson, B.M. Phillips, J. Newman, R.S. Tjeerdema, R. Fairley, H.M. Puckett, M. Stephenson, R.W. Smity, C.J. Wilson, and K.M. Taberski. 2001. Evaluation and use of sediment toxicity reference sites for statistical comparisons in regional assessments. Environmental Toxicology and Chemistry 20(6):1266-1275.

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Ingersoll, C.G., N.E. Kemble, J.L. Kunz, W.G. Brumbaugh, D.D. MacDonald, and D. Smorong. 2009. Toxicity of Sediment Cores Collected from Ashtabula River in Northeastern Ohio, USA, to the Amphipod Hyalella Azteca. Archives of Environmental Contamination and Toxicology. 5792: 315-329.

A4-2. City of New York Calculation of PRGs for Total PAH

Calculation of PRGs for Total PAH based on valid toxicity test data returned a PRG of 2,414 mg Total PAH/Kg TOC (145 ppm total PAH in bulk sediment assuming 6 percent TOC in Gowanus Canal) for the growth endpoint and 6,861 mg Total PAH/Kg TOC (412 ppm total PAH in bulk sediment assuming 6 percent TOC in Gowanus Canal) for the survival endpoint.

The City has calculated PRGs based on survival and growth of *Letpocheirus plumulosus* for Total PAHs in Gowanus Canal based on recently obtained sediment toxicity data (A4.4 Toxicity Tests: Summary of Methods and Results). These data are more reliable than the data used by EPA in their calculation of a Total PAH PRG. The EPA toxicity test data exist under a cloud of substantial uncertainty due to problems incurred in the laboratory testing of the sediments and the nature of the sediments tested.

A4-2.1. EPA Toxicity Test Results

Specifically, the prior EPA toxicity testing (see **A4-3 Critique of EPA Toxicity Test Data**) and PRG calculations based on them:

- Required three re-starts due to the poor health of test organisms;
- Exceeded recommended holding times for testing of *Leptocheirus plumulosus* by as many as 15 weeks;
- Failed to explain how the sediments were handled, stored, or manipulated during the long time periods between the various restarts;
- Did not explain or even acknowledge the confounding factors due to the oily and tarry nature of eight of the tested samples.

A4-2.2. City Toxicity Test Results

The City calculated PRGs for Total PAHs based on:

- EPA definitions of NOEC and LOEC;
- The results of 28 day toxicity testing using *Leptocheirus plumulosus* from the same station locations previously occupied and sampled by EPA;
- The results of recently of recently obtained chemical analysis of sediments form the same stations previously occupied and sampled by EPA;
- Application of the method cited by EPA in the FS Addendum for the derivation of PRGs (NAVFAC, 2010).

Smithers Viscient Laboratory conducted sediment toxicity tests (see **A4-4 Toxicity Tests: Summary of Methods and Results – Attachment A4-2**) on sediment samples collected from 12 site locations and 5 reference locations (Figure 1) during January, 2013. All toxicity tests began within recommended holding times of 2 weeks of collection. The City evaluated toxicity in the site samples based on a statistical comparison to the pooled results from the reference samples for three endpoints, reductions in survival, growth, and reproduction of the sediment invertebrate, *Leptocheirus plumulos*us.

Table A4.2.1 shows the toxicity test results. Seven (7) site samples (309, 310,313, 314, 315, 318, and 319) had zero percent survival. These are a continuous subset of stations in the middle reach of

Gowanus Canal with visibly oiled sediments. For these sites, sub-lethal endpoints for *L. plumulosus,* such as growth and reproduction, could not be measured.

Table A4.2.1. Toxicity Test Results – Comparison with Pooled Reference Site Results

Test Day 28			
Test Sample	**Mean Percent Survival (SD)**	**Mean Dry Weight per Amphipod in Milligrams (SD)**	**Mean # Offspring Per Adult (SD)**
Pooled Reference	**55(34)**	**1.0(0.37)**	**1.9(1.8)**
NYCDEP-GC-TX-303	30(17)	0.47(0.08)**	0.91(0.98)
NYCDEP-GC-TX-307A	2(3)*	NA	NA
NYCDEP-GC-TX-307B	30(19)	0.50(0.36)**	0(0)**
NYCDEP-GC-TX-309	0(0)*	NA	NA
NYCDEP-GC-TX-310	0(0)*	NA	NA
NYCDEP-GC-TX-313	0(0)*	NA	NA
NYCDEP-GC-TX-314	0(0)*	NA	NA
NYCDEP-GC-TX-315	0(0)*	NA	NA
NYCDEP-GC-TX-318	0(0)*	NA	NA
NYCDEP-GC-TX-319	0(0)*	NA	NA
NYCDEP-GC-TX-321	45(9)	0.72(0.28)	0.15(0.29)**
NYCDEP-GC-TX-324	79(20)	1.10(0.33)	1.06(0.85)
Reference Sites			
326	48(26)	0.88(0.45)	48
328	50(39)	0.92(0.43)	50
329	73(41)	1.33(0.29)	73
330	60(38)	1.01(0.44)	60
333	42(41)	0.85(0.17)	42

* Significantly reduced when compared to the Pooled Reference samples. Due to the reduction in survival, the sub-lethal endpoints for this test sample were omitted from further statistical comparisons.
** Significantly reduced when compared to the Pooled Reference samples.

A4-2.3. Calculation of Total PAH PRG

The City of New York calculated PRGs for TOC normalized total PAHs using the method cited in the FS Addendum (NAVFAC, 2010). Specifically, the City:

- Specified a toxicity test sample as toxic based on a statistical comparison to reference area samples;
- Used the measured concentrations of total PAHs normalized to synoptically obtained TOC at each toxicity test sample as the exposure concentration associated with that sample;
- Grouped all non-toxic samples by endpoint;
- Grouped all toxic samples by endpoint;

- Selected a NOEC from the sample with the highest concentration within the group of non-toxic samples;
- Selected a LOEC from the sample within the group of toxic samples that has the lowest concentration, but is greater than the maximum concentration within the group of non-toxic samples;
- Calculated the geometric means of the NOECs and LOECs for each COC by endpoint to provide a TOC normal PRG;
- Assumed 6 percent TOC in Gowanus Canal to convert the TOC normalized PRG to a bulk sediment total PAH PRG.

Table A4.2-2 (survival endpoint) and **Table A4.2-3** (growth endpoint) group the stations as toxic and non-toxic and show the associated Total PAH, TOC, and TOC normal PAH concentrations. Following the method described above, calculation of PRGs for Total PAH Based on valid toxicity test data returned a PRG of:

- 2,414 mg Total PAH/Kg TOC (145 ppm total PAH in bulk sediment assuming 6 percent TOC in Gowanus Canal) for the growth endpoint; and,
- 6,861 mg Total PAH/Kg TOC (412 ppm total PAH in bulk sediment assuming 6 percent TOC in Gowanus Canal) for the survival endpoint.

Table A4.2-2. Ecological PRG Development - Based on L. plumulosus Survival

Sample ID	Sample concentrations		
	Total PAHs (mg/kg)	TOC (ug/g)	Total PAH (mg/kg) TOC Normalized
Non-Toxic Samples			
303	437	100,000	4,370
307B	91	92,000	989
321	64	48,000	1,333
324	43	49,000	878
NOEC[(1)]			**4,370**
Toxic Samples			
307A	122	96,000	1,271
309	460	160,000	2,875
310	169	120,000	1,408
313	167	5200	32,115
314	6,149	120,000	51,242
315	2,129	81,000	26,284
318	1,508	140,000	10,771
319	936	82,000	11,415
LOEC[(2)]			**10,771**
Geometric Mean of NOEC and LOEC			**6,861**
Bulk Value (based on 6 percent TOC in Gowanus Canal)			**412**

1 Maximum concentration in a non-toxic sample.

2 Lowest concentration in a toxic sample that is greater than the maximum concentration in a non-toxic sample.

A4-2.4. Sources of Uncertainty

The nature of the toxicity data results in a small sample size to use in calculating a PRG for PAHs because:

- Most of the Gowanus Canal stations (seven of 12) cannot be used to estimate a PRG for PAHs because the sample exhibited visible oil in the lab. Therefore the test organisms were potentially affected by the physical effects of oil (e.g. interference with respiration, ingestion of oil) before the toxic effects of PAHs from uptake and exposure would occur;
- Among the remaining five (non-oily) stations, the low survival in the reference areas results in only one toxic sample (for survival endpoints) and only two toxic samples (for growth endpoint) in Gowanus Canal (relative to the pooled reference area sample);
- The survival in the reference area is low and highly variable.

Table A4.2-3. Ecological PRG Development - Based on L. plumulosus Growth

Sample ID	Sample concentrations		
	Total PAHs (mg/kg)	TOC (ug/g)	Total PAH (mg/kg) TOC Normalized
Non-Toxic Samples			
321	64	48,000	1,333
324	43	49,000	878
NOEC(1)			**1,333**
Toxic Samples			
303	437	100,000	4,370
307B	91	92,000	989
LOEC(2)			**4,370**
Geometric Mean of NOEC and LOEC			**2,414**
Bulk Value (based on 6% TOC in Gowanus Canal)			**145**
No Growth Data(3)			
307A	NA		
309	NA		
310	NA		
314	NA		
315	NA		
318	NA		
319	NA		

1. Maximum concentration in a non-toxic sample.
2. Lowest concentration in a toxic sample that is greater than the maximum concentration in a non-toxic sample.
3. Samples had zero survival and growth could not be measured.

References:

NAVFAC (Naval Facilities Engineering Command). 2010. Record of Decision: Site 2B – Area A Wetland, Naval Submarine Base – New London, Groton, Connecticut. August 2010.

A4-3. Critique of EPA Toxicty Test Data

The United States Environmental Protection Agency (EPA) offered a Preliminary Remediation Goal (PRG) of 7.8 ppm Total Polycyclic Aromatic Hydrocarbons (Total PAHs) based on test results using the organism, *Leptocheirus plumulosus*. However, the City recognized several sources of uncertainty in the execution of these tests and in the physical and chemical properties of the toxicity test sediment samples (see below).Therefore the City used the more certain results offered by EPA's sediment toxicity testing using the organism, *Nereis virens*. The City calculated a PRG of 85 ppm using these more certain *Nereis* data (using a different calculation method, EPA calculated a PRG of 289 ppm using these more certain data). The City notes that the 85 ppm total PAH value is within the range of estimated PRGs from other sites (adjusted for organic carbon content of Gowanus Canal sediments) based on a review of accessible PRGs from other sites nation-wide and calculated for bottom dwelling invertebrate receptors.

Subsequent to technical presentations from the City, EPA requested that the City calculate a range of PRGs using the uncertain *Leptocheirus* test data. This calculated range was 25 ppm Total PAHs to 39 ppm Total PAHs. EPA has recently changed the PRG from 7.8 ppm to 25 ppm Total PAHs subsequent to considering the City's calculations using the *Leptocheirus* test data. The City, however, emphasizes that these *Leptocheirus* tests exist under a cloud of substantial uncertainty due to problems that occurred during the execution of these tests in the laboratory and due to the physical nature of the sediments collected from Gowanus Canal. Specifically:

- The tests had to be restarted three times due to poor health of the test organisms. In response to a query from the City, EPA explained that the laboratory used an alternative source of test organisms to conduct the third attempt.
- The EPA toxicity test report specifically claims to follow EPA Guidance (EPA, 2001) but apparently exceeded recommended holding times for the *Leptocheirus* toxicity tests. The three "restarts" apparently led EPA to exceed the holding times recommended for this toxicity test in the EPA testing manual (EPA, 2001)which recommends two weeks holding times and always less than 8 weeks to minimize test variability and effects on toxicity (in either direction). EPA guidance also recommends that if "*If whole-sediment toxicity tests are started more than 2 weeks after collection, it is desirable to conduct additional characterizations of sediment to evaluate possible effects of storage on sediment"* (EPA, 1994). The EPA toxicity test data report (EPA, 2011) shows that the tests on samples collected on June 17, 2011 began on October 14 and terminated on November 11, 2011. This time frame indicates that the toxicity testing began 17 weeks after collection of samples and therefore exceeds EPA recommended holding times by as many as 15 weeks.
- It is unclear from either EPA's Baseline Ecological Risk Assessment or EPA's laboratory reports how the laboratory made up the second and third restarted samples. Specifically, there is no explanation of how the sediments were handled between "restarts." EPA has not explained whether the laboratory resampled the parent sample three times or re-used previously distributed sample for the second and third restart. The absence of this important procedural detail sheds uncertainty on whether the EPA Guidance (EPA, 2001) recommendation to minimize disturbance of the sample was followed.

The physical and chemical nature of the toxicity testing samples also inject significant uncertainties into EPA's interpretation of the toxicity test data and their use of these data to calculate a PRG. An examination of the sediment collection logs (EPA, 2010) reveals that the sediment samples were often characterized by having sheens, petroleum odors, tar-like odors, and high PID readings (indicating VOCs in the samples). The presence of these physical impacts (oils and tars in the tested sediments) has the clear potential to confound the interpretation of any possible relationships between the toxicity test results and the concentrations of specific chemical compounds. Specifically:

- Among the twelve site sediment samples submitted for toxicity testing, eight exhibited sheens and odors;
- The three most toxic samples had "heavy" sheens and odors. Sample 313 (which EPA omitted from their PRG calculation) is characterized as having a PHC (petroleum hydrocarbon) odor and sheen on sediment and water. Sample 314 had a heavy sheen and "tar-like odor." Sample 315 had a "tar-like odor" and sheen with very high PID readings (28.3 ppm). It is unclear to the City why one would submit heavily tarred or oiled sediments for a toxicity test given the potential for the physical impact (oil or tar) to confound the test results.
- The fact that sample 313 which had a "heavy" petroleum sheen and relatively low PAH concentrations exemplifies the manner in which such obvious physical impacts confound the interpretation of the toxicity test results.
- The samples exhibiting the lowest toxic responses were, with one exception, those samples that did not exhibit sheens and odors. In other words, the case can be made that the toxic responses are tracking the oil in the sediments rather than the PAH concentrations. This confounding influence of the oils or tars may help to explain why EPA could not develop a statistically significant dose response relationship between toxicity and PAH concentrations.

Additionally, the City notes that:

- All the samples that the City's analysis indicates are not toxic relative to EPA's estimated NOAEC had no sheens or slight sheen (sample 303). The City notes that the toxicity appears to track the sheens, a physical impact unrelated to PAH concentrations.
- The sediment logs inform the discussion of PAH sources. For example, the samples with the highest concentrations of PAHs (by orders of magnitude) were those samples with "heavy" sheens and "tar-like" odors. In contrast, samples with petroleum odors had much lower PAH concentrations.

As a result of these uncertainties, the City does not recommend using the *Leptocheirus* toxicity data to calculate a PRG. Rather, the City recommends the more certain results offered by EPA's *Nereis* sediment toxicity test. The EPA PRG of 25 ppm is still based on the uncertain *Leptocheirus* test data, and therefore the City recognizes the value as insufficiently robust.

Rather than use an uncertain data set, the City plans to re-sample the five EPA reference stations in Gowanus Bay and the 12 previously sampled Gowanus Canal stations for toxicity testing using *Leptocheirus plumulosus*, sediment chemistry for the Gowanus Canal Contaminants of Concern, and sediment physical-chemical properties (Total Organic Carbon and grain size). The City will use these data to re-calculate a PRG based on sediment toxicity.

References:

EPA, 1994. Assessment and Remediation of Contaminated Sediments (ARCS) Program, Assessment Guidance Document Chapter 6, US Environmental Protection Agency. 1994. ARCS Assessment Guidance Document. EPA 905-B94-002. Chicago, Ill.: Great Lakes National Program Office.

EPA, 2001. EPA 600/R-01/020, March 2001, Method for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-associated Contaminants with the Amphipod Leptocheirus plumulosus, Office of Research and Development, Western Ecology Division, U.S. Environmental Protection Agency

EPA, 2010. Gowanus Canal Remedial Investigation Report, Appendix D-02 Surface Sedimetn Sampling Field Forms.

EPA, 2011. Appendix K Ecological Risk Assessment, Combined Screening Level and Baseline Ecologial Risk Assessment Data Appendix: TOXICOLOGICAL EVALUATION OF SEDIMENT SAMPLES Gowanus Canal Superfund Site Brooklyn, New York Bioassay Testing 28 Day Leptocheirus plumulosus Survival, Growth and Reproduction Toxicity Tests, Envirosytems, 2010.

A4-4. Toxicity Tests: Summary of Methods and Results

This appendix describes the results of the 28 day *Leptocheirus plumulosus* sediment toxicity tests conducted on a subset of sediment samples collected in January 2013. Appendix A1 provides the details of the sampling methods.

A4-4.1. Toxicity Test Sampling Locations and Observations

The City obtained samples for toxicity testing from the 17 stations previous sampled by EPA for toxicity testing (EPA, 2011). These included twelve locations in Gowanus Canal and five reference area stations. **Figure A4.4.1** shows the sampling locations. **Attachment A4-1** provides the field notes and photographs of samples for each toxicity test station sampled. These notes provide the data and time of sampling, the observable physical and biological characteristics of the sample, and observations of anthropogenic material, oils, and odors associated with each sample.

A4-4.2. Toxicity Testing Methods

Smithers Viscient Laboratory conducted the sediment toxicity tests on the 17 samples sediment samples according to standard methods and began all toxicity tests within EPA recommended holding times of 2 weeks of collection. **Attachment A4-2** provides the laboratory methods, toxicity test results, and the results of the statistical comparison between (1) individual controls and site samples, (2) pooled controls and site samples, (3) individual reference areas and site samples, and (4) pooled reference area samples and site samples.

A4-4.3. Toxicity Test Results

The City evaluated toxicity in the site samples based on a statistical comparison to the pooled results from the reference samples for three endpoints, reductions in survival, growth, and reproduction of the sediment invertebrate, *Leptocheirus plumulos*us. **Table A4.4.1** shows the results of these statistical comparisons along with station-specific information on the chemical and physical characteristics of the tested samples. **Figures A4.4.2 and A4.4.3** show the geographic distribution of toxicity based on survival and toxicity based on growth respectively.

The reference area samples returned relatively average low survival (pooled average 55%) and high standard deviations (**Table A4.4.1**).

During field collection oil was apparent in samples from all Gowanus Canal stations and reference area station 333 (**Attachment A4-1**). At the initiation of the laboratory testing, seven site samples (309, 310,313, 314, 315, 318, and 319) had visibly oiled sediments. The toxicity tests from these samples had zero percent survival. For these samples, sub-lethal endpoints for *L. plumulosus,* (growth and reproduction) obviously could not be measured. **Figure A4.4.2** shows that these oily, low survival samples are a continuous subset of stations in the middle reach of Gowanus Canal. These data indicate that the large middle reach of Gowanus Canal is so physically altered due to the presence of separate phase oil that the complete mortality observed there is probably due to the physical impact of oils on the test organisms rather than being due to the uptake and exposure to particle bound contaminants such as PAHs.

Note that the zero survival in seven of the Gowanus Canal samples as a result of oil and the very low survival in sample 307A reduce the number of stations available to assess the potential toxicity based on growth or reproduction to four site stations.

Figure A4.4.3 shows the distribution of toxicity in Gowanus Canal stations based on the sublethal endpoint, growth. (The analysis of the sublethal endpoints from station 307A could not be statistically evaluated relative to the pooled reference samples due to the low (2 percent) survival in that sample).

The sediments in the lower reach of Gowanus Canal appear to be non-toxic (based on growth and survival).

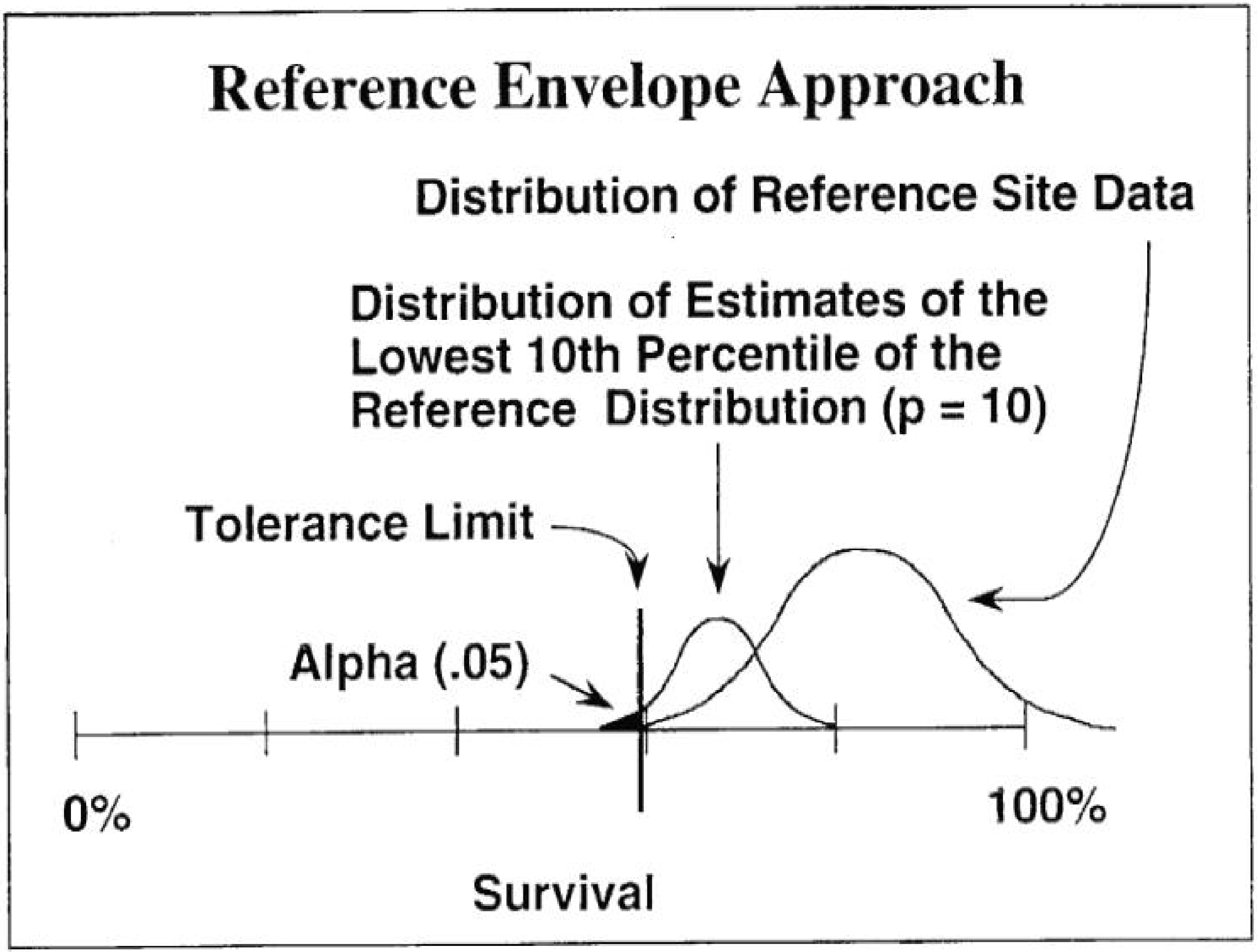
The City did not further evaluate the toxicity based on reproduction due to the typically high variability in this endpoint (standard deviations approach 100 percent of the mean).

Table A4.4.1. Toxicity Test Results Summary

Test Sample	Mean Percent Survival (SD)	Growth [Mean Dry Weight per Amphipod, mg] (SD)	Mean # Offspring Per Adult (SD)	Oil Observed in Lab Sample	Oil Observed in Field Sample	Total PAH mg/kg	TOC ug/g	PAH mg/kg (TOC normalized)
Lab Control 1	**81(18)**	**1.16(0.58)**	**3.7(2.1)**					
Lab Control 2	**97(4)**	**1.44(0.40)**	**5.2(1.4)**					
Sample Sites								
NYCDEP-GC-TX-303	30(17)	0.47(0.08)**	0.91(0.98)	no	yes	437	100,000	4,370
NYCDEP-GC-TX-307A	2(3)*	NA	NA	no	yes	122	96,000	1,271
NYCDEP-GC-TX-307B	30(19)	0.50(0.36)**	0(0)**	no	yes	91	92,000	989
NYCDEP-GC-TX-309	0(0)*	NA	NA	yes	yes	460	160,000	2,875
NYCDEP-GC-TX-310	0(0)*	NA	NA	yes	yes	169	120,000	1,408
NYCDEP-GC-TX-313	0(0)*	NA	NA	yes	yes	167	5,200	32,115
NYCDEP-GC-TX-314	0(0)*	NA	NA	yes	yes	6,149	120,000	51,242
NYCDEP-GC-TX-315	0(0)*	NA	NA	yes	yes	2,129	81,000	26,284
NYCDEP-GC-TX-318	0(0)*	NA	NA	yes	yes	1,508	140,000	10,771
NYCDEP-GC-TX-319	0(0)*	NA	NA	yes	yes	936	82,000	11,415
NYCDEP-GC-TX-321	45(9)	0.72(0.28)	0.15(0.29)**	no	yes	64	48,000	1,333
NYCDEP-GC-TX-324	79(20)	1.10(0.33)	1.06(0.85)	no	yes	43	49,000	878
Reference Sites								
326	48(26)	0.88(0.45)	1.5(1.4)	no	no	11	33,000	343
328	51(39)	0.92(0.43)	1.6(1.3)	no	no	38	25,000	1,508
329	91(9)	1.3(0.29)	3.4(2.0)	no	no	6	30,000	193
330	60(38)	1.08(0.38)	2.7(2.3)	no	no	11	36,000	300
333	45(29)	0.89(0.13)	0.32(0.24)	no	yes	55	54,000	1,019
Pooled Reference	**55(34)**	**1.0(0.37)**	**1.9(1.8)**					

* Significantly reduced when compared to the Pooled Reference samples. Due to the reduction in survival, the sub-lethal endpoints for this test sample were omitted from further statistical comparisons.

** Significantly reduced when compared to the Pooled Reference samples



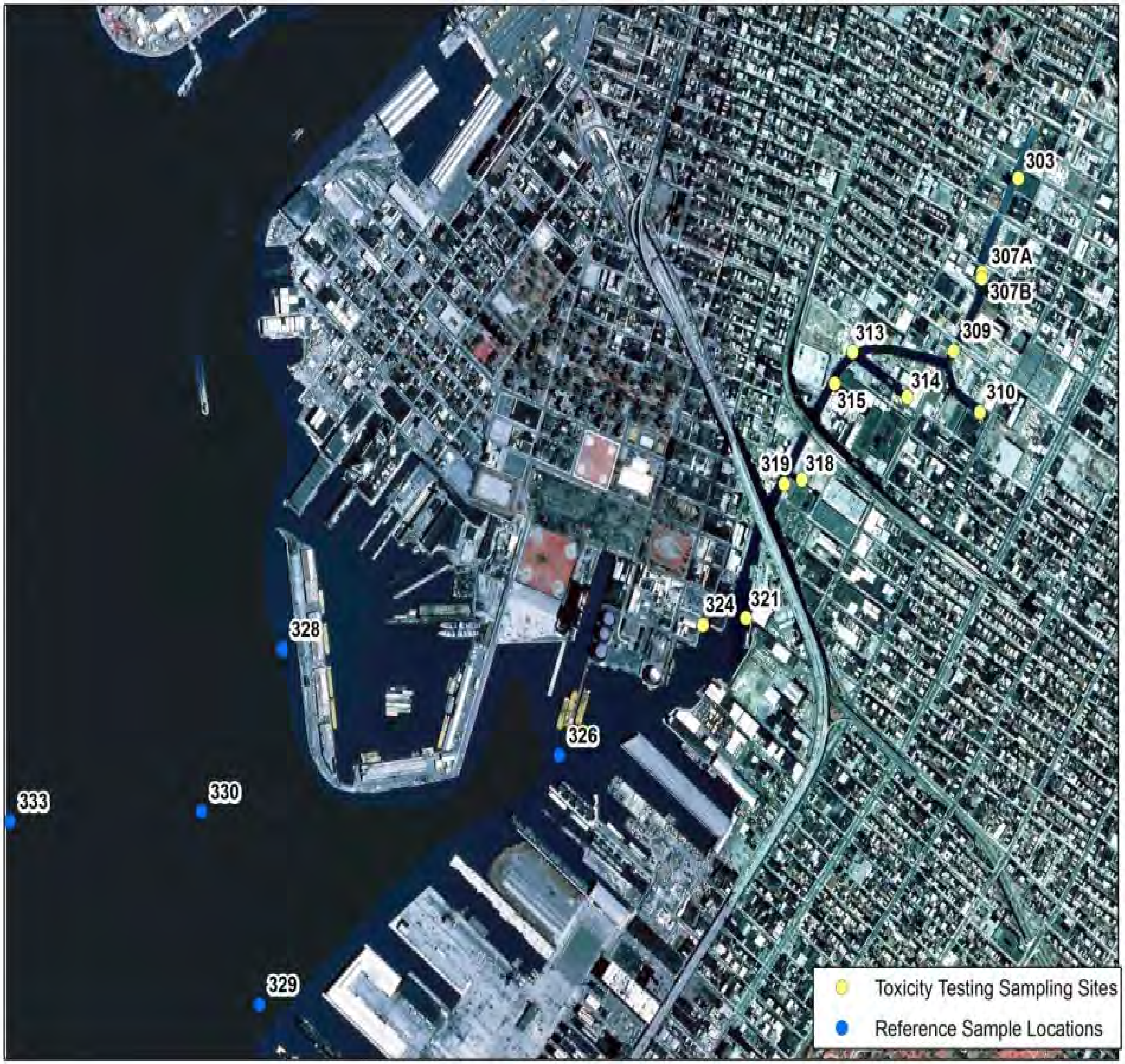
NYC Environmental Protection

Concept of the Tolerance Limit
(from Hunt et al. 1998)

Gowanus Canal Superfund Site

Figure A4.1-1

April 2013



Environmental Protection

Toxicity Test Sampling Stations

Gowanus Canal Superfund Site

Figure A4.4-1

April 2013

Distribution of Toxicity Measured as Survival in Gowanus Canal

Gowanus Canal Superfund Site

Figure A4.4-2

April 2013

Note: oily stations and station 307A could not be evaluated for toxicity based on growth due to very high mortality

Environmental Protection

Distribution of Toxicity in Gowanus Canal Based on Growth

Gowanus Canal Superfund Site

Figure A4.4-3

April 2013

Attachment A4-1: Field Sampling Notes

Gowanus Canal Sediment Sampling for Toxicity Testing: Field Notes

Sediment sampling was conducted in the Gowanus Canal from January 9 through January 12, 2013 for risk assessment purposes. This attachment summarizes observations on sediment quality and provides photographs of each sediment sample from the canal.

Seventeen sampling stations were occupied in the Canal and just outside the Canal.
At each sampling station the first acceptable grab was characterized in terms of surface characteristics, sediment type, organic matter, anthropogenic material/debris, biota, odor, sheen, moisture, density, color, and grab quality and number of attempts. If subsequent grabs were different in nature from the first one, the differences were noted.

The remainder of this attachment provides data sheets and photographs from each sampling station. Stations are documented in the order in which samples were collected.

Gowanus Canal Sediment Sampling

Station ID GC-319 **Date Collected** 1-9-13 Time: 09:42

Recovery Depth 4-6" (Petite Ponar grabs 3/4 full + full)

Field Observations

Depositional surface veneer and surface characteristics Surface mostly smooth w/ fine gray-black silt layer. Some mottling;

Sediment Type SILT w trace vf sand

Organic Matter Present in all grabs. Twigs, leaves, fragments

Anthropogenic Material/Debris Hair-like material; trace of small plastic-like or ribbon-like fragments

Biota 1 2" crab (possibly green crab) at surface of grab on one of the 4 grabs

Odor Moderate-strong petroleum-like odor

Sheen Moderate rainbow sheen

Moisture, Density, Color Comments Moist, moderately stiff, black

Grab Quality, Number of Attempts Good quality grabs - surface intact

Other Notes

Station 319
Date 1-9-13
Time 10:15

Gowanus Canal Sediment Sampling

Station ID GC - 321 **Date Collected** 1-9-13 Time: 11:15

Recovery Depth Full petite ponars approx. 6" (150 mm)

Field Observations

Depositional surface veneer and surface characteristics No

Sediment Type SILT with some fine sand

Organic Matter Some organic matter - fragments, twigs, leaves

Anthropogenic Material/Debris None observed

Biota None observed, but furrows at surface possibly associated w/ biota

Odor Petroleum-like odor

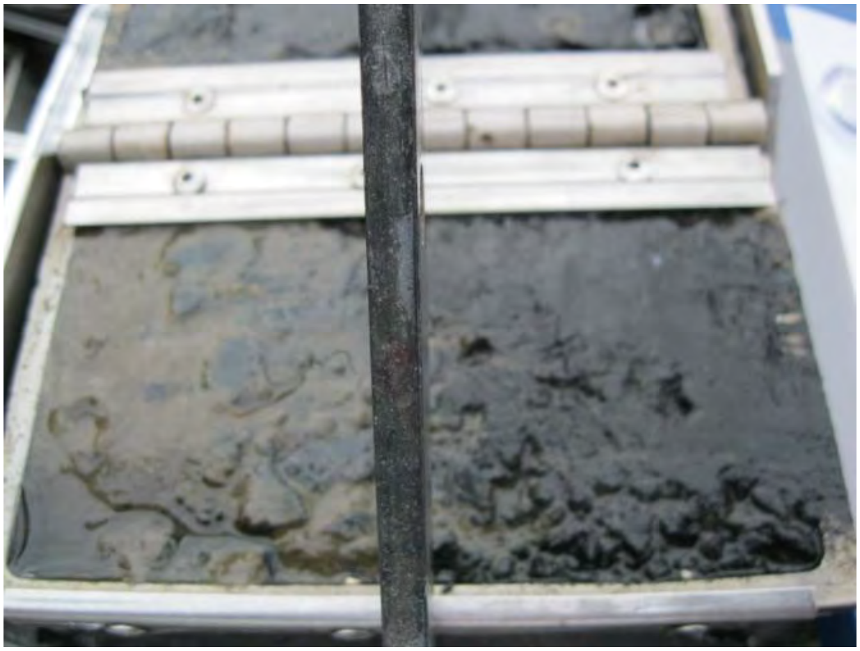
Sheen Minor- moderate sheen in sediment, and sheen in overlying water

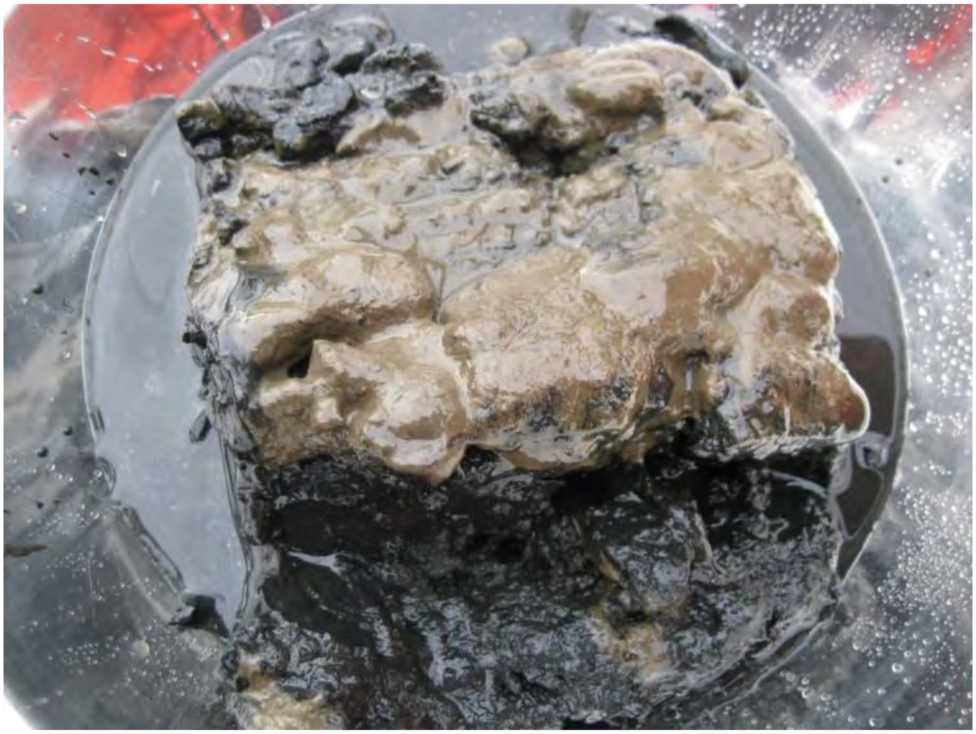
Moisture, Density, Color Comments Wet, very soft, black sediment. One grab had surface sediment layer (≈ 2-5 mm) of brown-gray silt overlying black sediment

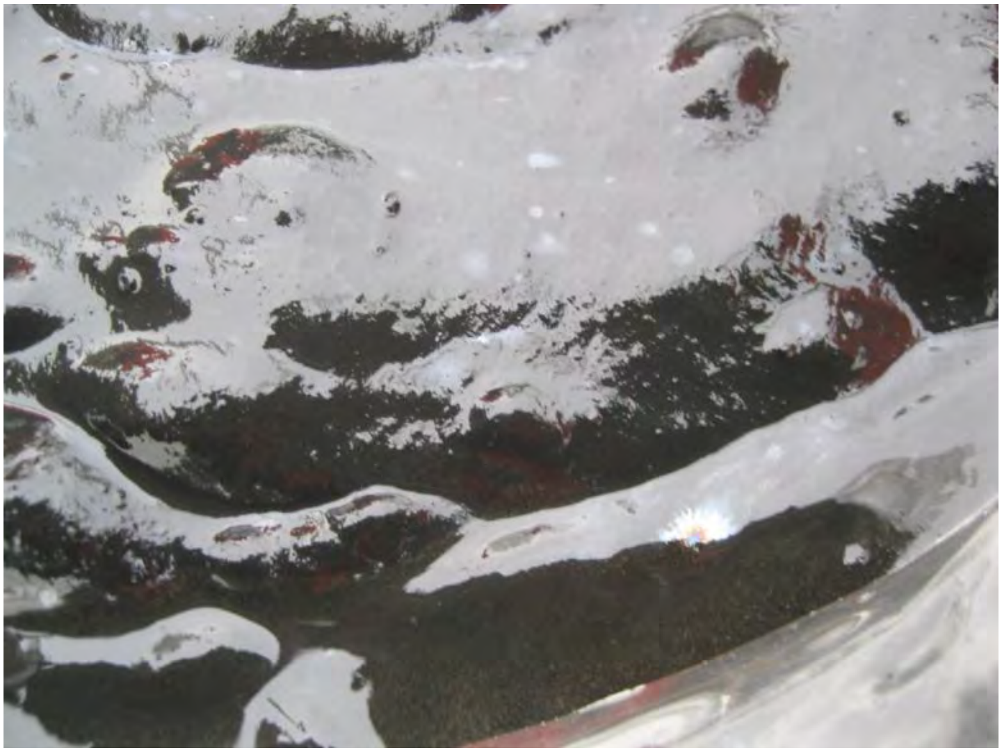
Grab Quality, Number of Attempts Good quality - flat surface, full grabs

Other Notes In subsequent grabs, sediment had mottled area where surface sediment was brown-gray silt (approx 1-4 mm thick)

Station 321
Date 1-9-13
Time 11:15







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Gowanus Canal Sediment Sampling

Station ID GC-324

Date Collected 1-9-13

Recovery Depth Approx. 6"

Time: 11:55

Field Observations

Depositional surface veneer and surface characteristics Thin (2-6 mm) layer brown-gray silt at surface; surface smooth and flat

Sediment Type Brown-gray SILT at 2-6 mm, grades to black SILT with trace fine sand at approx. 2-6 mm

Organic Matter Trace organic matter

Anthropogenic Material/Debris Small amount anthropogenic debris - becomes evident on mixing

Biota None observed

Odor Moderate petroleum-like odor

Sheen Sheen florets in overlying water + in sediment

Moisture, Density, Color Comments Wet, very soft, black but moderately stiff

Grab Quality, Number of Attempts Flat surface and full grab, 1 attempt

Other Notes

Station 324
1-09-13
11:55

Gowanus Canal Sediment Sampling

Station ID GC-309

Date Collected 1-9-13

Recovery Depth Approx. 6"

Time! 12:56

Field Observations

Depositional surface veneer and surface characteristics Surface layer appears less smooth than most samples, possibly due to fibrous organic matter mixed with sediment

Sediment Type SILT with some fine sand

Organic Matter Hair-like fibers, leaves, fragments, lots of fibrous-looking material at surface of grab

Anthropogenic Material/Debris Hair- or wire-like fibers; ribbon-like debris

Biota None observed

Odor Moderate petroleum-like

Sheen Moderate Rainbow Sheen

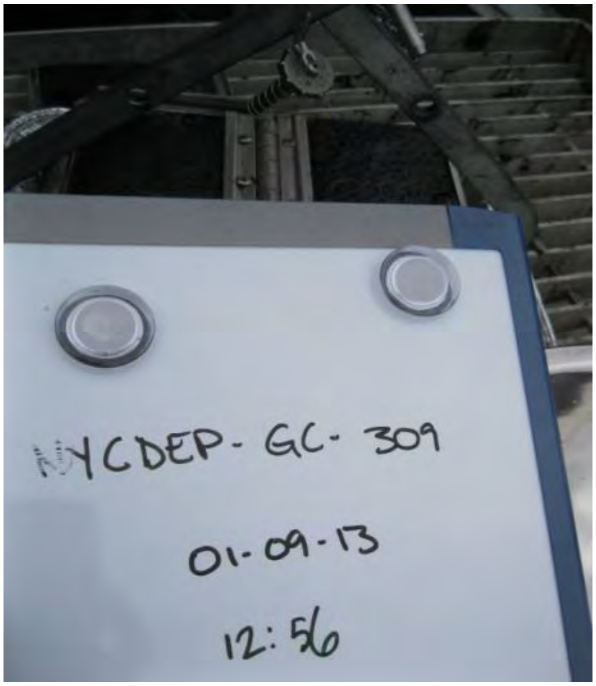
Moisture, Density, Color Comments Very wet, soft, almost liquid, non-cohesive, black

Grab Quality, Number of Attempts Grab intact; 1 attempt

Other Notes

Station 309

1-09-13
12:56



Gowanus Canal Sediment Sampling

Station ID GC-310

Date Collected 1-9-13

Time: 13:50

Recovery Depth 6"

Field Observations

Depositional surface veneer and surface characteristics

Sediment Type SILT w trace vF sand; grades to SILT with layers of brown/gray SILT-CLAY w: some vF sand

Organic Matter Leaves, twigs, hair-like fibers

Anthropogenic Material/Debris Not evident in sample but visible in viscinity

Biota None observed

Odor Strong H_2S-like

Sheen Heavy sheen on sample and on surface water in viscinity of sample

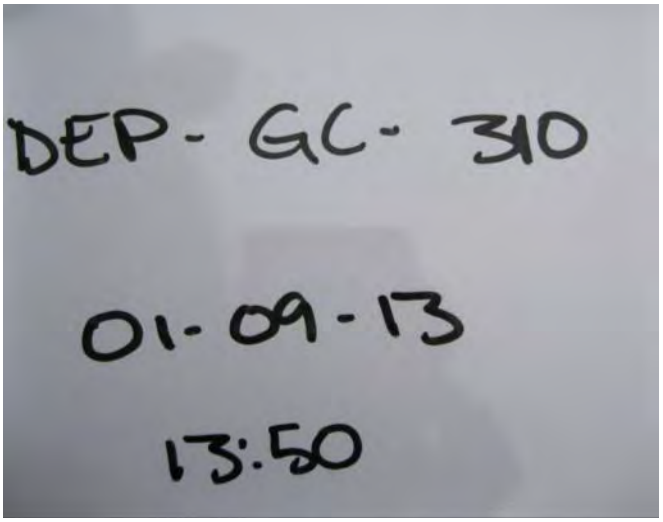
Moisture, Density, Color Comments Moist, soft + poorly consolidated black sediment

Grab Quality, Number of Attempts Flat surface, full grab - required care in order to avoid over-filling as sediment was soft

Other Notes Station at easternmost spur on the canal - relatively little flushing

- Tar-like residue on sampling equipment. Also dark brown + rainbow sheen on sampling bowls after washing with Alconox. Required extra scrubbing with hexane.

Station 310
1-9-13
13:50



DEP- GC- 310

01-09-13

13:50

Gowanus Canal Sediment Sampling

Station ID GC-314 **Date Collected** 1-9-13

Recovery Depth 6" Time : 14:43

Field Observations

Depositional surface veneer and surface characteristics Surface oily; soft, flat sediment with organic debris

Sediment Type SILT with trace fine sand. Mottled areas at surface with brown oily SILT entrained in larger sample

Organic Matter Moderate - heavy organic debris

Anthropogenic Material/Debris Some debris - ribbon- or straw- like in shape; possibly textile or rubber material

Biota None observed

Odor Strong H_2S- like odor

Sheen Moderate - heavy sheen on sediment and overlying water

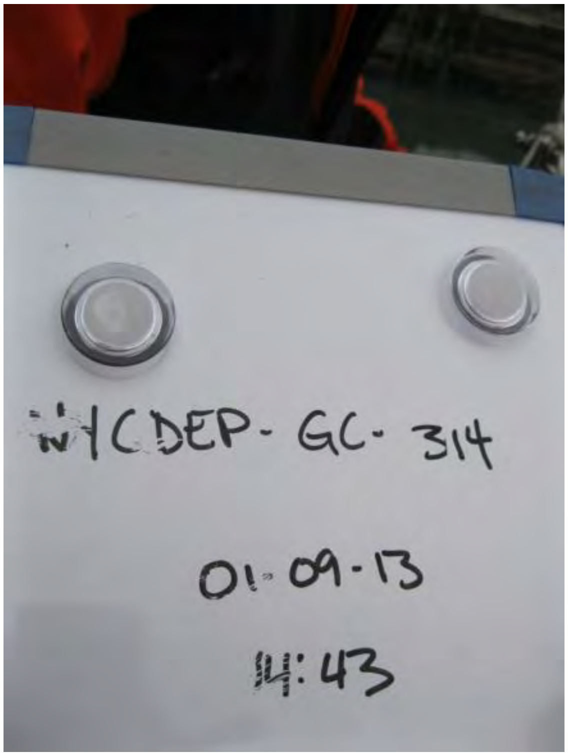
Moisture, Density, Color Comments Very moist, wet, soft, poorly consolidated, black

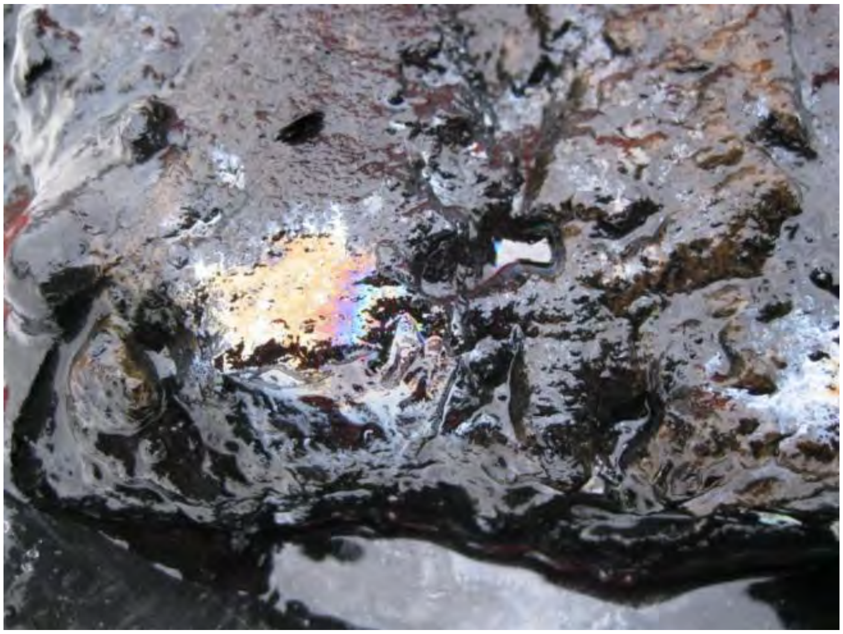
Grab Quality, Number of Attempts Flat surface, overlying water intact 1 attempt

Other Notes Thick sheen surface water appears oily or waxy in nature.

- Tar-like residue on sampling equipment required heavy scrubbing with hexane

Station 314
1-09-13
14:43






Sampling Area


Waxy sheen on surface water in vicinity of grab

Station 313
1-10-13
09:05

Large piece of aggregate material in grab

Station 315
1-10-13
10:15

Gowanus Canal Sediment Sampling

Station ID GC-326 1 **Date Collected** 1-10-13

Recovery Depth 6" Time: 11:46

Field Observations

Surface characteristics Flat, gray-brown fine sediment, with some coarse sand at surface

Sediment Type 1ST Grab: Gray-black SILT with some Fine sand
2nd Grab Top layer (≈ 4-7 mm) is SILT with some coarse sand + gravel. Grades to SILT-CLAY at ≈ 5-18 mm.
3rd Grab: slightly medium coarse sandy SILT. ([illegible]).

Organic Matter Trace to some organic matter especially in Top layer of sediment (little to none observed in deeper layers)

Anthropogenic Material/Debris No

Biota No

Odor No

Sheen No - but one grab did show red-color deposits on surface - See photograph. Doesn't appear to be a sheen - perhaps microbial mat(?)

Moisture, Density, Color Comments Stiff, well-consolidated sediment. Likely higher clay content than samples collected inside the Canal.

Grab Quality, Number of Attempts Good quality grabs - surface intact + overlying water in place

Other Notes

Station 326
1-10-13
11:46

Gowanus Canal Sediment Sampling

Station ID GC-329

Date Collected 1-10-13

Time: 13:15

Recovery Depth 6" all grabs

Field Observations

Surface characteristics smooth, flat brown-gray silt w/ trace vf sand. No sheen evident at surface.

Sediment Type Brown-gray silt w/ trace vf sand. Grades to gray silt w trace vf sand at 3-6 mm.

Organic Matter None observed

Anthropogenic Material/Debris None observed

Biota —

Odor No odor

Sheen No sheen apparent on any grab

Moisture, Density, Color Comments Moderately stiff, well consolidated material in all grabs.

Grab Quality, Number of Attempts 1st attempt successful on all grabs

Other Notes

Station 329
1-10-13
13:15

Gowanus Canal Sediment Sampling

Station ID GC-318

Date Collected 1-11-2013

Time: 07:20

Recovery Depth 6", 4", 1", 6"

Field Observations

Surface characteristics Gray-brown silty sediment w/ organic matter; Slight sheen apparent at surface.

Sediment Type SILT w some medium-coarse sand

Organic Matter Moderate -> large amounts. Twigs, leaves, fragments

Anthropogenic Material/Debris Small + large ribbon-like debris; some pieces have a balloon-like texture + weight (appears similar to a deflated balloon)

Biota None observed

Odor Strong odor - H_2S and/or petroleum-like odor

Sheen Yes Moderate to heavy sheen in all grabs. Sheen becomes apparent on mixing + is visible on surface sediment

Moisture, Density, Color Comments Very moist, non-cohesive

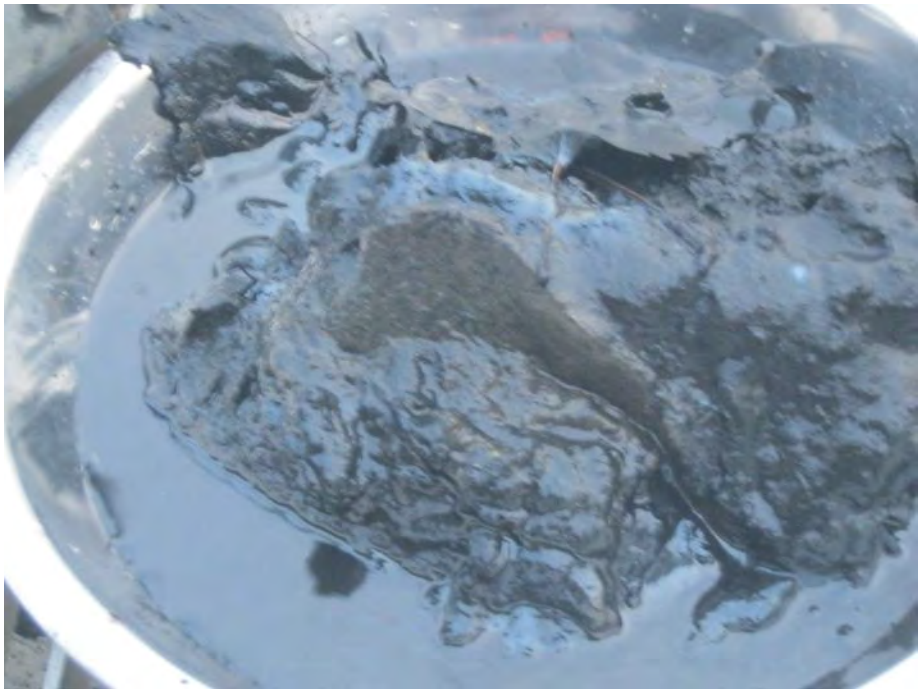
Grab Quality, Number of Attempts Several grabs required to achieve acceptable samples (12 attempts for 4 acceptable, one of which was not quite full).

Other Notes Tar-like material was not evident in samples but was evident on sampling equipment after sampling (during decon, tar became evident)

-> Intertidal Station - dry at low tide

-> Screw on petite ponar was dropped during sampling but retrieved at low tide when exposed + could access on foot.

Station 318
1-11-13
07:20



Gowanus Canal Sediment Sampling

Station ID GC-330 **Date Collected** 1-11-13

Recovery Depth 4-6" dep. on grab Time: 09:00

Field Observations

Surface characteristics 1st Grab: Surface flat, slightly furrowed, shell fragments + pebbles on surface; 2nd grab has a thin (2-5 mm) layer brown SILT w/ some shell fragments + sand, 3rd grab is gray-brown silt with coarse sand + shell fragments

Sediment Type Surface layer is SILT w/ shell fragments + sand. Grades to black SILT w/ some clay and medium sand

Organic Matter Leaves, twigs, fragments

Anthropogenic Material/Debris Not observed

Biota No live animals; shell fragments at surface

Odor No

Sheen No

Moisture, Density, Color Comments Moist, cohesive, stiff sediment

Grab Quality, Number of Attempts Several grabs (3-7) required for each acceptable one

Other Notes

Station 330
1-11-13
09:00

Gowanus Canal Sediment Sampling

Station ID GC-333 **Date Collected** 1-11-13

Recovery Depth 3-4" dep. on grab Time: 10:10

Field Observations

Surface characteristics Shells + shell fragments (mainly soft shell clams + blue mussels). Light sheen on 1 grab; other grabs had brown-gray silt at surface, along with heavy shell material

Sediment Type Sandy SILT with some clay. One grab had a 2-5mm surface layer of silt, grading to silt/clay at 5mm.

Organic Matter Twigs, fragments

Anthropogenic Material/Debris Ribbon-like debris

Biota No live animals but lots of Mya arenaria + Mytilus edulis shells + fragments. Also noted 2 Polychaete worm tubes, but no worms.

Odor —

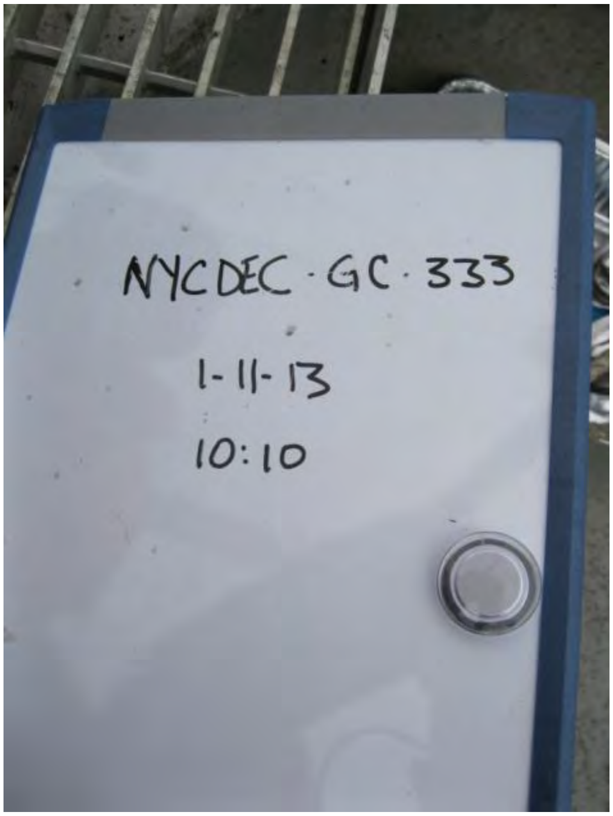
Sheen Yes - light sheen on 2 of the grabs, became apparent on mixing the sample

Moisture, Density, Color Comments Moist, very stiff, cohesive at depth, surface layer less stiff (more sandy + shells)

Grab Quality, Number of Attempts Poor quality - no grabs full. Required 5-10 attempts per acceptable grab.

Other Notes

Station 333
1-11-13
10:10



Gowanus Canal Sediment Sampling

Station ID GC-328 **Date Collected** 1-11-13

Recovery Depth 3-4" dep. on grab. Time: 13:15
None Full 6"

Field Observations

Surface characteristics Gray-black sandy material with lots of shell + shell fragment plus pebbles

Sediment Type Fine to medium SAND

Organic Matter Twigs, shells,

Anthropogenic Material/Debris —

Biota 2 live quahogs (2" and 2 1/2")
Polychaete worm tubes
Lots of shells + fragments but no other live animals
- besides the 2 quahogs

Odor —

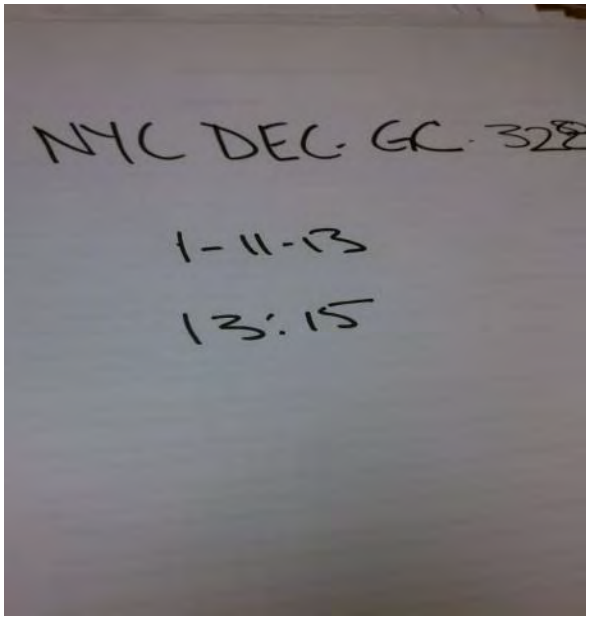
Sheen —

Moisture, Density, Color Comments Poorly consolidated, sandy, black to brown/black

Grab Quality, Number of Attempts No full grabs. 3-4 attempts per grab accepted

Other Notes Station is deep (~ 40 ft) but close to breakwater

Station 328
1-11-13
13:15



NYC DEC. GC. 328

1-11-13

13:15

Gowanus Canal Sediment Sampling

Station ID GC-307A **Date Collected** 1-12-13

Recovery Depth 6" all grabs Time: 10:00

Field Observations

Surface characteristics Wet, loose, black-gray; high organics
Fine material

Sediment Type SILT

Organic Matter Leaves, twigs, fragments

Anthropogenic Material/Debris —

Biota —

Odor Heavy H_2S odor

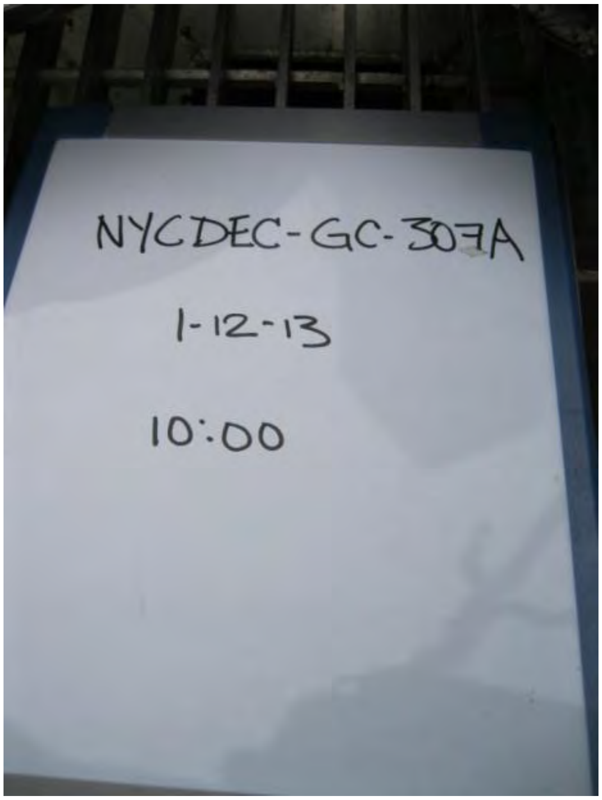
Sheen Heavy rainbow sheen

Moisture, Density, Color Comments Wet, poorly consolidated,
black, loose

Grab Quality, Number of Attempts Good quality, several attempts

Other Notes Above 3rd St. Bridge - skiff required
for access

Station 307A
1-12-13
10:00


NYCDEC-GC-307A

1-12-13

10:00


NYCDEC-GC-307A

Gowanus Canal Sediment Sampling

Station ID GC- 307 B **Date Collected** 1-12-13

Recovery Depth 6" Time: 11:00

Field Observations

Surface characteristics Surface shows organics (leaves) shiny veneer, sheen + sheen florets

Sediment Type SILT w some vf sand. One grab showed thin (2-4 mm) layer brown silt overlying black SILT w/ very fine sand

Organic Matter High OM - twigs, leaves

Anthropogenic Material/Debris —

Biota —

Odor Strong H2S - like odor

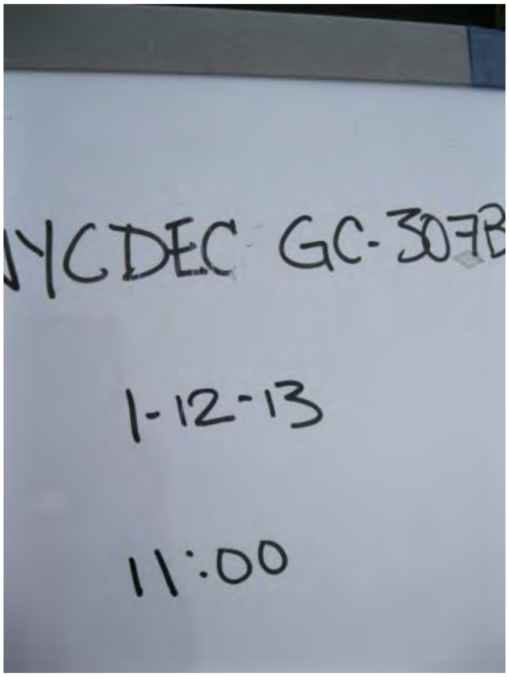
Sheen Moderate - heavy rainbow

Moisture, Density, Color Comments Wet, moderately stiff, black

Grab Quality, Number of Attempts Acceptable grabs each attempt, reported by samplers in skiff

Other Notes Above 3rd St. Bridge - required skiff for access. Dead rat observed floating nearby while sampling

Station 307B
1-12-13
11:00



Gowanus Canal Sediment Sampling

Station ID GC-303

Date Collected 1-12-13

Recovery Depth 6"

Time: 12:46

Field Observations

Surface characteristics Shiny, smooth + mottled areas w/ gray metallic blotches + possibly bacterial in nature

Sediment Type SILT w/ trace VF sand

Organic Matter Heavy organic matter - twigs, leaves, fragments

Anthropogenic Material/Debris In visinity but not in grabs

Biota —

Odor Strong H_2S odor

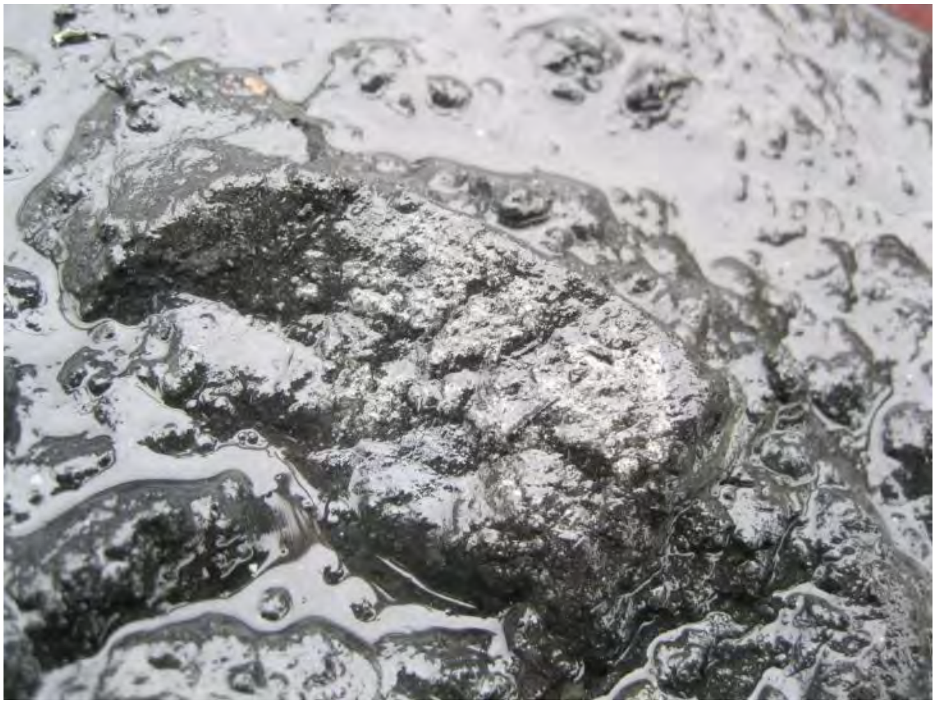
Sheen Heavy Sheen

Moisture, Density, Color Comments Wet moderately stiff, black to gray-black

Grab Quality, Number of Attempts 3 attempts per acceptable; full grabs when acceptable

Other Notes

Station 303
1-12-13
12:46



Attachment A4-2: Smithers Viscient Summary Report

SUMMARY REPORT

Chronic Toxicity Evaluation of Sediment Samples using *Leptocheirus plumulosus*

Author

Christian R. Picard

Study Completed On

27 March 2013

Submitted To

Louis Berger Group, Inc.
565 Taxter Road, Suite 510
Elmsford, New York 10523

Performing Laboratory

Smithers Viscient
790 Main Street
Wareham, Massachusetts 02571-1037

Laboratory Project ID

Smithers Viscient Study No. 14054.6100

GOOD LABORATORY PRACTICE NON-COMPLIANCE STATEMENT

At the request of the sponsor, the study was not conducted in accordance with the Good Laboratory Practice standards of any regulatory body. However, the data and summary report for **"Chronic Toxicity Evaluation of Sediment Samples using *Leptocheirus plumulosus*"** have been reviewed and approved by the study director, and considered technically sound.

SMITHERS VISCIENT

Christian R. Picard
Study Director

27 Mar 13
Date

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KEY STUDY PERSONNEL

The following Smithers Viscient personnel were responsible for the conduct of the work and reporting of the study results.

Christian R. Picard	Study Director
Ruth Clark	Assistant Biologist
Jennifer Kenney	Assistant Biologist
Christopher A. Malcolm	Assistant Biologist
Adriana Lafave	Assistant Biologist
Brian Snow	Assistant Biologist
Andrea M. Soares	Technical Report Writer
Mark A. Cafarella	Director, Ecotoxicology

EXECUTIVE SUMMARY

The following is a summary of testing performed with the estuarine amphipod (*Leptocheirus plumulosus*) to evaluate sediment sample toxicity. The test sediments were shipped by Louis Berger Group, Inc., Elmsford, New York on 12 January 2013 and received at Smithers Viscient, Wareham, Massachusetts on 14 January 2013. Seventeen test samples (identified as NYCDEP-GC-TX-303, NYCDEP-GC-TX-307A, NYCDEP-GC-TX-307B, NYCDEP-GC-TX-309, NYCDEP-GC-TX-310, NYCDEP-GC-TX-313, NYCDEP-GC-TX-314, NYCDEP-GC-TX-315, NYCDEP-GC-TX-318, NYCDEP-GC-TX-319, NYCDEP-GC-TX-321, NYCDEP-GC-TX-324, NYCDEP-GC-TX-326, NYCDEP-GC-TX-328, NYCDEP-GC-TX-329, NYCDEP-GC-TX-330 and NYCDEP-GC-TX-333) were collected. Sediment samples NYCDEP-GC-TX-326, NYCDEP-GC-TX-328, NYCDEP-GC-TX-329, NYCDEP-GC-TX-330 and NYCDEP-GC-TX-333 were designated reference samples. The sediment samples were stored refrigerated and wet-pressed through a 2-mm sieve prior to use in testing.

In addition, Smithers Viscient collected natural marine sediment from Little Harbor located in Wareham, Massachusetts to serve as the Laboratory Control sediment. This sediment was wet pressed through a 0.25-mm sieve prior to use in testing. Two control groups (each with five replicates) were set up along with the sediment test and reference samples. These control groups were designated as Laboratory Control 1 and Laboratory Control 2.

The procedures used during the conduct of this study followed Smithers Viscient Test Method No. 101904 entitled "28-Day Static-Renewal Toxicity Test with Estuarine Amphipods (*Leptocheirus plumulosus*) to Meet U.S. EPA Guidelines". The methods described in this test method meet the testing requirements of EPA Guideline: "Methods for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-Associated Contaminants with the Amphipod *Leptocheirus plumulosus*" (U.S. EPA, 2001). The test method followed during the conduct of this test is attached in Appendix 1.

A 96-hour reference test with *L. plumulosus* was completed on 5 February 2013. Cadmium chloride was the reference toxicant used. The population of organisms used to initiate the reference test was from the same population of organisms used to initiate all of test sediments. The 96-hour LC50 for cadmium and *L. plumulosus* was calculated to be 3.0 mg cadmium/L. Appendix 2 contains the control chart for this reference test and previously conducted reference tests. The reference test completed on 5 February 2013 fell within the acceptable two standard deviation range established from the calculated LC50 values.

A summary of the water quality characteristics of overlying water during the 28-day exposure is presented in Table 1 and Table 2. Water quality remained acceptable throughout the 28-day exposure period. Throughout the exposure period, dissolved oxygen concentrations were greater than or equal to the required 60% of saturation in all samples, with one exception (see note, Table 1). Water temperature measured daily in the exposure vessels and continuous temperature monitoring in an auxiliary vessel set up in the water bath used to house the test vessels established a range of 20 to 26 ^{o}C throughout the exposure. Ammonia concentrations, measured in overlying water during the exposure, were ≤ 5.2 mg/L in all samples.

A summary of the *Leptocheirus plumulosus* survival, growth and reproduction during the 28-day exposure period and statistical comparisons is presented in Table 3. The percent survival, growth and reproduction for organisms exposed to Laboratory Control 1 averaged 81%, 1.16 mg per amphipod and 3.7 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to Laboratory Control 2 averaged 97%, 1.44 mg per amphipod and 5.2 offspring per adult, respectively. The performance of the control organisms met the minimum survival criteria for this type of study (i.e., ≥ 80% survival and measurable growth and reproduction); therefore, the results of the testing were deemed to be acceptable.

The percent survival, growth and reproduction for organisms exposed to reference sample NYCDEP-GC-TX-326 averaged 48%, 0.88 mg per amphipod and 1.5 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to reference sample NYCDEP-GC-TX-328 averaged 51%, 0.92 mg per amphipod and 1.6 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to reference sample NYCDEP-GC-TX-329 averaged 91%, 1.3 mg per amphipod and 3.4 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to reference sample NYCDEP-GC-TX-330 averaged 60%, 1.08 mg per amphipod and 2.7 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to reference sample NYCDEP-GC-TX-333 averaged 45%, 0.89 mg per amphipod and 0.32 offspring per adult, respectively.

The percent survival, growth and reproduction for organisms exposed to test sample NYCDEP-GC-TX-303 averaged 30%, 0.47 mg per amphipod and 0.91 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to test sample NYCDEP-GC-TX-307A averaged 2%, 0.41 mg per amphipod and 0 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to test sample NYCDEP-GC-TX-307B averaged 30%, 0.50 mg per amphipod and 0 offspring per adult, respectively. The percent survival for organisms exposed to test samples NYCDEP-GC-TX-309, NYCDEP-GC-TX-310, NYCDEP-GC-TX-313, NYCDEP-GC-TX-314, NYCDEP-GC-TX-315, NYCDEP-GC-TX-318 and NYCDEP-GC-TX-319 was 0%. The percent survival, growth and reproduction for organisms exposed to test sample NYCDEP-GC-TX-321 averaged 45%, 0.72 mg per amphipod and 0.15 offspring per adult, respectively. The percent survival, growth and reproduction for organisms exposed to test sample NYCDEP-GC-TX-324 averaged 79%, 1.10 mg per amphipod and 1.06 offspring per adult, respectively.

CONCLUSIONS

Results established that the laboratory control organism survival, growth and reproduction were within the range of acceptance criteria. Consequently, the exposure system provided conditions which were appropriate for amphipod survival, growth and reproduction in order to assess any toxic effects.

SUMMARY OF TEST CONDITIONS

Chronic Toxicity Evaluation of Sediment Samples using *Leptocheirus plumulosus*

DATE SAMPLES RECEIVED:	14 January 2013
TEST DATES:	24 January to 21 February 2013
TEST TYPE:	Whole-sediment toxicity test
TEMPERATURE:	20 to 26 °C
LIGHT INTENSITY:	720 to 970 lux
PHOTOPERIOD:	16 hours light. 8 hours dark
TEST CHAMBER SIZE:	1000 mL
SEDIMENT VOLUME:	Approximately 120 mL
OVERLYING WATER VOLUME:	750 mL
RENEWAL OF TEST SOLUTIONS:	400 mL overlying water renewed three times per week
AGE/SIZE OF TEST ORGANISMS:	Neonates; those passing through a 0.60-mm and being captured on a 0.25-mm sieve
NUMBER OF ORGANISMS PER TEST CHAMBER:	20
NUMBER OF REPLICATE TEST CHAMBERS PER TREATMENT:	5
NUMBER ORGANISMS/SAMPLE:	100
FEEDING:	2.0 mL of flaked fish food suspension per test chamber three times per week for days 0 through 13, 4.0 mL three times per week for days 14 through 27
AERATION:	Gentle oil-free aeration (2 to 3 bubble/second)

TEST CONCENTRATION:	100% (no dilutions)
TEST DURATION:	28 days
ENDPOINTS:	Survival, growth (dry weight) and reproduction
TEST ACCEPTABILITY:	Minimum mean control survival of 80% and measurable growth/reproduction

Table 1. Water quality summary (dissolved oxygen, temperature, pH and salinity) for the *Leptocheirus plumulosus* 28-day exposure.

Sample Identification	**Dissolved Oxygen (mg/L)**	**Temperature (°C)[a]**	**pH**	**Salinity (‰)**
Laboratory Control 1	6.4 - 7.6	20 - 26	7.5 - 8.1	20 - 22
Laboratory Control 2	4.8 - 7.3	20 - 26	7.3 - 8.0	20 - 24
NYCDEP-GC-TX-303	5.4 - 7.1	20 - 26	7.6 - 8.5	20 - 22
NYCDEP-GC-TX-307A	6.1 - 7.2	20 - 26	7.0 - 8.5	20 - 22
NYCDEP-GC-TX-307B	5.5 - 7.3	20 - 26	7.0 - 8.5	20 - 21
NYCDEP-GC-TX-309	4.7 - 7.3	20 - 26	7.3 - 8.6	20 - 21
NYCDEP-GC-TX-310	5.7 - 7.1	20 - 26	7.2 - 8.5	20 - 21
NYCDEP-GC-TX-313	5.8 - 7.2	20 - 26	7.6 - 8.4	20 - 21
NYCDEP-GC-TX-314	5.9 - 7.2	20 - 26	7.6 - 8.5	20 - 21
NYCDEP-GC-TX-315	6.2 - 7.1	20 - 26	7.7 - 8.5	20 - 21
NYCDEP-GC-TX-318	5.9 - 7.2	20 - 26	7.8 - 8.6	20 - 21
NYCDEP-GC-TX-319	6.0 - 7.3	20 - 26	7.6 - 8.5	20 - 21
NYCDEP-GC-TX-321	6.0 - 7.3	20 - 26	7.9 - 9.0	20 - 21
NYCDEP-GC-TX-324	5.8 - 7.0	20 - 26	7.0 - 8.4	20 - 21
NYCDEP-GC-TX-326	6.0 - 7.2	20 - 26	7.7 - 8.2	20 - 21
NYCDEP-GC-TX-328	6.2 - 7.3	20 - 26	7.2 - 8.5	20 - 21
NYCDEP-GC-TX-329	6.2 - 7.2	20 - 26	7.8 - 8.3	20 - 21
NYCDEP-GC-TX-330	3.6[b] - 7.2	20 - 26	7.5 - 8.7	20 - 21
NYCDEP-GC-TX-333	6.3 - 7.3	20 - 26	7.7 - 8.2	20 - 21

[a] Continuous temperature monitoring in an auxiliary vessel set up in the water bath used to house the test vessels established a temperature range of 20 to 26 °C throughout the exposure period.

[b] During water quality measurements on test day 25, it was discovered that the aeration in replicate E of this treatment was off. Aeration was restored and a dissolved oxygen measurement of 7.1 mg/L was obtained for this vessel one hour later.

Table 2. **Summary of overlying water ammonia concentrations measured during the *Leptocheirus plumulosus* 28-day exposure.**

Sample Identification[a]	**Overlying Water Ammonia (mg/L)**	
	Day 0	**Day 28**
Laboratory Control 1	1.4	0.14
Laboratory Control 2	1.3	0.15
NYCDEP-GC-TX-303	4.0	0.11
NYCDEP-GC-TX-307A	1.2	≤ 0.10
NYCDEP-GC-TX-307B	2.8	0.26
NYCDEP-GC-TX-309	1.7	0.11
NYCDEP-GC-TX-310	3.6	0.42
NYCDEP-GC-TX-313	≤ 0.10	≤ 0.10
NYCDEP-GC-TX-314	3.1	0.12
NYCDEP-GC-TX-315	5.2	≤ 0.10
NYCDEP-GC-TX-318	1.3	0.77
NYCDEP-GC-TX-319	1.8	≤ 0.10
NYCDEP-GC-TX-321	1.6	0.13
NYCDEP-GC-TX-324	1.5	0.22
NYCDEP-GC-TX-326	0.34	≤ 0.10
NYCDEP-GC-TX-328	0.75	≤ 0.10
NYCDEP-GC-TX-329	0.99	≤ 0.10
NYCDEP-GC-TX-330	1.9	≤ 0.10
NYCDEP-GC-TX-333	0.36	≤ 0.10

[a] Samples removed from a composite of replicate A through E. Values presented are rounded to two significant figures.

Table 3. Summary of survival, growth and reproduction of *Leptocheirus plumulosus* at termination of the 28-day exposure.

Test Sample ID	Test Day 28		
	Mean Percent Survival (SD)	**Mean Dry Weight per Amphipod in Milligrams (SD)**	**Mean Number of Offspring per Amphipod (SD)**
Laboratory Control 1	81 (18)	1.16 (0.58)	3.7 (2.1)
Laboratory Control 2	97 (4)	1.44 (0.40)	5.2 (1.4)
Pooled Control[a]	89 (15)	1.3 (0.49)	4.5 (1.9)
NYCDEP-GC-TX-326	48 (26)	0.88 (0.45)	1.5 (1.4)
NYCDEP-GC-TX-328	51 (39)	0.92 (0.43)	1.6 (1.3)
NYCDEP-GC-TX-329	91 (9)	1.3 (0.29)	3.4 (2.0)
NYCDEP-GC-TX-330	60 (38)	1.08 (0.38)	2.7 (2.3)
NYCDEP-GC-TX-333	45 (29)	0.89 (0.13)	0.32 (0.24)
Pooled Reference[b]	55 (34)	1.0 (0.37)	1.9 (1.8)
NYCDEP-GC-TX-303	30 (17)[cde]	0.47 (0.08)[iko]	0.91 (0.98)
NYCDEP-GC-TX-307A	2 (3)[cdefgn]	0.41 (0.23)[k]	0 (0)[kmp]
NYCDEP-GC-TX-307B	30 (19)[cde]	0.50 (0.36)[iko]	0 (0)[ikmop]
NYCDEP-GC-TX-309	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-310	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-313	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-314	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-315	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-318	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-319	0 (0)[cdefghjln]	NA (NA)	NA (NA)
NYCDEP-GC-TX-321	45 (9)[cde]	0.72 (0.28)[i]	0.15 (0.29)[ioq]
NYCDEP-GC-TX-324	79 (20)	1.10 (0.33)	1.06 (0.85)[rst]

SD = Standard Deviation
NA = Not Applicable

[a] Pooled Control = Laboratory Control 1 and Laboratory Control 2.
[b] Pooled Reference = NYCDEP-GC-TX-326, NYCDEP-GC-TX-328, NYCDEP-GC-TX-329, NYCDEP-GC-TX-330 and NYCDEP-GC-TX-333.
[c] Significantly reduced compared to Laboratory Control 1. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[d] Significantly reduced compared to Laboratory Control 2. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[e] Significantly reduced compared to Pooled Control. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[f] Significantly reduced compared to reference sample NYCDEP-GC-TX-326. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[g] Significantly reduced compared to reference sample NYCDEP-GC-TX-329. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[h] Significantly reduced compared to reference sample NYCDEP-GC-TX-328. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[i] Significantly reduced compared to reference sample NYCDEP-GC-TX-329.
[j] Significantly reduced compared to reference sample NYCDEP-GC-TX-330. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[k] Significantly reduced compared to reference sample NYCDEP-GC-TX-330.
[l] Significantly reduced compared to reference sample NYCDEP-GC-TX-333. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[m] Significantly reduced compared to reference sample NYCDEP-GC-TX-333.
[n] Significantly reduced compared to Pooled Reference Sample. Due to the reduction in survival, the sublethal endpoints for this test sample were omitted from further statistical comparisons.
[o] Significantly reduced compared to Pooled Reference Sample.
[p] Significantly reduced compared to reference sample NYCDEP-GC-TX-328.
[q] Significantly reduced compared to reference sample NYCDEP-GC-TX-326.
[r] Significantly reduced compared to Laboratory Control 1.
[s] Significantly reduced compared to Laboratory Control 2.
[t] Significantly reduced compared to Pooled Control.

REFERENCES

U.S. EPA, 2001. Methods for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-Associated Contaminants with the Amphipod *Leptocheirus plumulosus*. Office of Research and Development. Washington. DC EPA/600/R-01/020.

APPENDIX 1

Test Method- 28-Day Static-Renewal Toxicity Test with Estuarine Amphipods (*Leptocheirus plumulosus*) to Meet U.S. EPA Guidelines

1.0 OBJECTIVE

The objective of this study is to determine the chronic toxicity of sediment samples to estuarine amphipods (*Leptocheirus plumulosus*) during a 28-day exposure. Amphipods are exposed to the sediment sample to assess survival, growth and number of young per surviving adult on test day 28 (test termination). The procedures described in this test method generally meet the standard procedures described in "Methods for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-Associated Contaminants with the Amphipod *Leptocheirus plumulosus*" (U.S. EPA, 2001).

2.0 MATERIALS AND METHODS

2.1. TEST ORGANISMS

2.1.1. **Species -** The estuarine amphipod, *Leptocheirus plumulosus*, is used to conduct the 28-day toxicity test. The neonate amphipods used to initiate the 28-day test are the same size and age and are those amphipods that pass through a 0.6 mm sieve and retained on a 0.25 mm sieve.

2.1.2. **Source -** The neonate amphipods are obtained from in-house cultures maintained at Smithers Viscient Laboratories or an outside supplier. The neonate amphipods will be held under the same conditions as testing (i.e., salinity 20 ± 2°C, temperature 25 ± 2 °C).

2.1.3. **Feeding -** While being maintained in the culture prior to the test, neonate amphipods are fed a flaked fish food suspension *ad libitum* each day. During the test, each exposure vessels is fed a flaked fish food suspension (10 mg/mL) three times per week (following renewal of overlying water). On test day 0 through 13, 2.0 mL of the flaked fish food suspension (10 mg/mL) is added to each exposure vessel. On days 14 through 27, 4.0 mL of the flaked fish food suspension (10 mg/mL) is added to each exposure vessel.

2.1.4. **Handling -** Wide-bore pipets and 0.25 mm stainless steel mesh sieves are used to isolate and transfer the neonate amphipods to the test vessels, taking care to minimize possible stress due to handling. Amphipods that are damaged or dropped during transfer are not used.

2.1.5. **Reference Test -** A 96-hour reference test, water-only exposure, using cadmium chloride may be conducted on a sub-population of organisms (from the same population used to initiate the test) within 30 days of the study. The health of the test population is assessed using the LC50 from the reference test.

2.2. PHYSICAL SYSTEM

2.2.1. **Sediment Samples -** Sediment samples (both test and reference sites) should be shipped to Smithers Viscient Laboratories. Upon receipt at the laboratory, sample containers are inspected for leakage or damage and the sample identity is recorded. If storage is required, the samples are refrigerated at approximately 2-8 °C. Prior to use, all sediment samples are pressed through a sieve (either a 1.0 or 2.0 mm sieve) to remove debris, large clumps of sediment, large predators, indigenous amphipods and to facilitate removal of offspring at termination of the test. Laboratory control sediment, collected by the testing laboratory, will be pressed through a 0.25 mm sieve to remove debris, large clumps of sediment, large predators, indigenous amphipods and to facilitate removal of offspring at termination of the test. The laboratory control sediment is included in the test to evaluate performance of the test organisms and exposure system. The test should be initiated within approximately 14 days of sediment collection.

2.2.2. **Test Chambers -** The test chambers used in the toxicity test are 1000 mL glass vessels that are chemically clean. Each jar contains 2 cm of sediment (approximately 120 mL) and 750 mL of overlying water. Test vessels will be covered with a plastic plate or lid during the test minimize evaporation of the overlying water. Each test vessel is labeled with the appropriate sample ID and replicate. Test vessels are cleaned by an appropriate method to remove residue of test material previously used (i.e., acid to remove metals and bases; detergents and organic solvents to remove organic compounds) and rinsed several times using tap water.

2.2.3. **Overlying Water -** Overlying water used in this test will be natural, filtered seawater from the Cape Cod Canal. The water will be filtered through a series of polypropylene core filters as fine as 5-µm and heated to the required test temperature. Salinity and pH of each new batch of seawater will be measured to ensure that these parameters will be within the normal acceptable ranges. The seawater will be diluted to a salinity of 20 ± 2°C with laboratory well water prior to use in culture and testing. The salinity and pH of the overlying water batches will be monitored on each batch following dilution with laboratory well water. Periodic analysis of representative samples of the overlying water source will be conducted to ensure the absence of potential toxicants, including pesticides, PCBs and selected toxic metals, at concentrations which may be harmful to the test organisms.

2.2.4. **Control Sediment** - Laboratory control sediment, will be collected from a site, known to be free of contamination and supports a local population of amphipods.

2.3. TEST PROCEDURES

2.3.1. **Test Concentration -** Each sediment sample is tested in five replicates, as 100% whole sediment (no dilutions). Sediment from one or more uncontaminated reference sites may be included in the test to evaluate the survival, growth (dry weight) and reproduction potential of the test organisms in non-contaminated sediment from the approximate site area. The laboratory control sediment is also tested in five replicates. Twenty amphipods per replicate (100 per sediment sample or reference control) are used to initiate the test.

2.3.2. **Test Initiation -** The day before test initiation (day -1) test sediments and laboratory control sediment are added to the test vessels. The overlying water is added gently to prevent resuspension of the sediment layer in the water column. This allows the sediment and water to equilibrate prior to addition of the test organisms.

At test initiation (day 0), neonate amphipods are removed from culture and twenty amphipods are impartially selected and pipeted into each replicate test or control vessel. This procedure is repeated until all vessels contain twenty amphipods. Test vessels are inspected within 2 hours after amphipods are introduced to ensure organisms are not trapped in the surface tension. Organisms trapped in the surface tension are removed and replaced with new amphipods.

2.3.3. **Renewal of Overlying Water -** During the 28-day study, the overlying water is renewed by siphoning 400 mL of the overlying water and replacing it with fresh seawater three times per week. The siphoning and replacement of overlying water is done carefully so as to not disturb the sediment layer.

2.3.4. **Photoperiod -** The test vessels are illuminated at a light intensity of 500 to 1000 lux using a combination of fluorescent bulbs. A 16-hour light, 8-hour dark photoperiod is maintained with an automatic timer.

2.3.5. **Measurement of Water Quality Variables -** At test initiation and test termination, temperature, pH, dissolved oxygen (DO) concentration and salinity in the overlying water are measured in each replicate test vessel. Temperature, DO, pH and salinity are measured daily in one replicate test vessel of each sample and control. These additional measurements are alternated between replicates on a daily basis. Ammonia concentrations are measured at test initiation and at test termination in a composite sample of overlying water from each replicate vessel of each sample and control. Temperature is monitored continuously in the water bath using a minimum-maximum thermometer. Temperature extremes are recorded daily.

2.3.6. **Dissolved Oxygen -** To prevent total dissolved oxygen from dropping below 4.4 mg/L (60% saturation at 25°C and 20°C), aeration (with oil-free air) is maintained throughout the exposure at a rate of approximately 1 to 3 bubbles per second with a glass pipette.

2.3.7. **Temperature -** Water temperature of the test solutions is maintained at 25 ± 2°C by conducting the study in a temperature controlled water bath.

2.3.8. **Biological Data -** Survival of the adult amphipods is determined in each test vessel at test termination by sieving the sediment, through a 0.60 mm and 0.25 mm sieve, to remove all surviving adult amphipods (retained on the 0.60 mm sieve) and young produced (retained on the 0.25 mm sieve). All surviving adult amphipods for each replicate vessel are then to a tared weigh boat and dried overnight at 60 ± 5°C. Following drying, the samples are cooled to room temperature and weighed on an analytical balance to the nearest 0.01 mg.

Young amphipods are removed from the 0.25 mm sieve and transferred to a labeled sample jar. Sufficient alcohol (a 70% ethanol solution is used) and 3.0 milliliters of concentrated Rose Bengal solution (1 mg/mL) is added to the sample jar to preserve and stain the offspring until they can be counted. Reproduction is reported as number of young per surviving adult amphipod in each replicate vessel.

2.3.9 **Acceptability Criteria -** The percent survival of adult amphipods in the control should be $\geq$80 % after 28 days of exposure and measurable growth and reproduction should be observed in laboratory control vessels. Professional judgment will be used to determine if the exposure is acceptable based on the results of the laboratory control and reference site samples.

3.0 CALCULATIONS

Survival, growth, number of young per surviving adult amphipod for each sediment sample is compared to the survival, growth, number of young per surviving adult amphipod in the appropriate reference sediment sample or laboratory control sediment for determination of significant adverse effects.

The survival, growth, number of young per surviving adult amphipod of each sediment sample will be tested for normality and homogeneity of variance using the appropriate qualifying test. If the data set passes these two tests, then a parametric method will be used to evaluate the results of each test sample for significant adverse effects. If the data set fails the test for normality and homogeneity of variance, then a non-parametric method will be used to determine significant adverse effects. If necessary, values obtained as a proportion (i.e., percent survival) will be transformed (e.g., arcsine square root) prior to analysis.

4.0 REPORTING

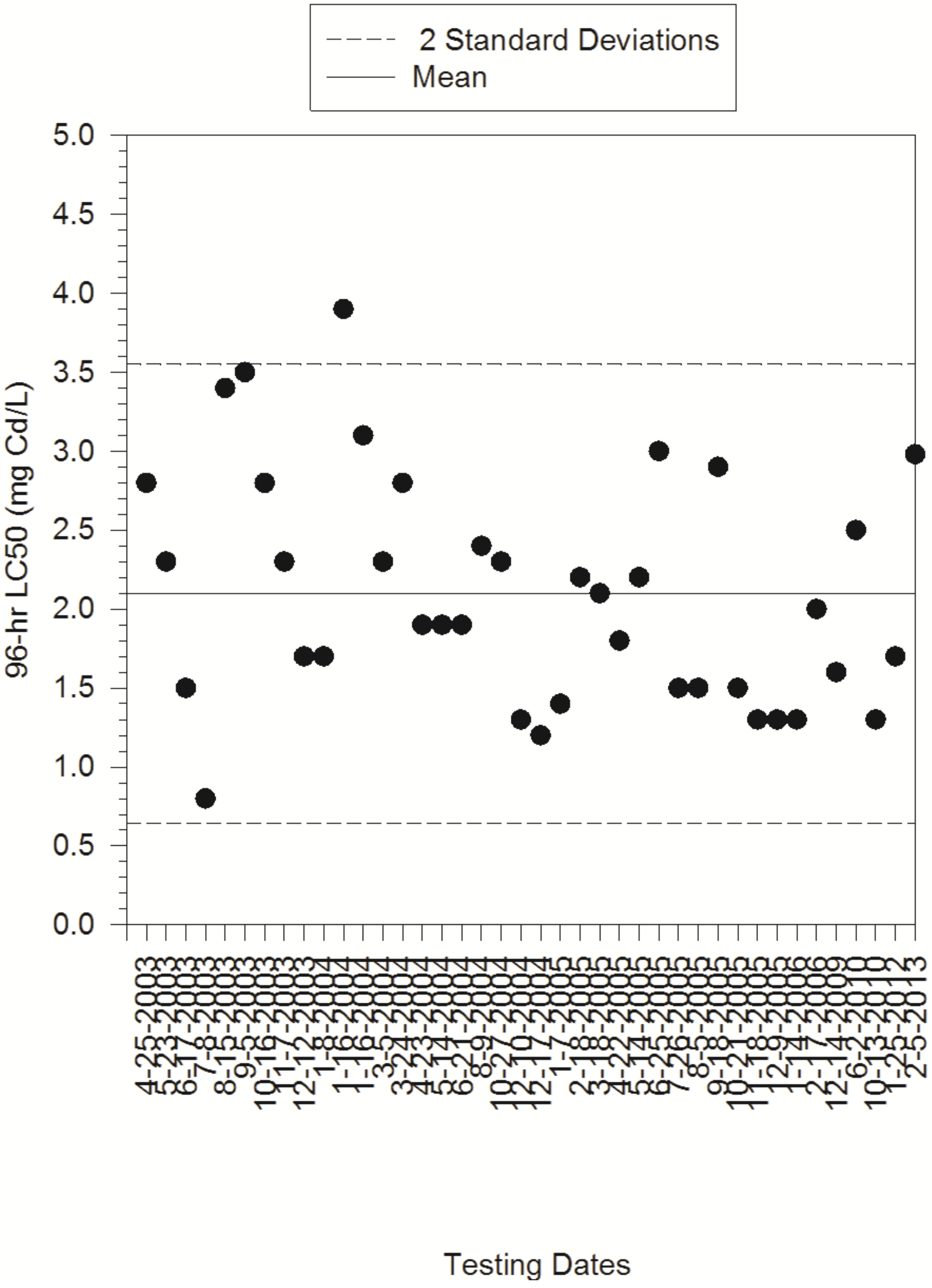
The raw data and summary report are reviewed by the Study Director. The test results will be presented in an outline format on a per sample basis.

5.0 REFERENCES

U.S. EPA. 2001. Methods for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-Associated Contaminants with the Amphipod *Leptocheirus plumulosus*. Office of Research and Development. Washington, DC EPA/600/R-01/020.

APPENDIX 2

Leptocheirus plumulosus Reference Testing with Cadmium



Attachment B: Letter from Eric Stein, Principal Scientist, Southern California Coastal Water Research Project to Angela Licata, Deputy Commissioner for Sustainability, NYCDEP (2013)

SOUTHERN CALIFORNIA COASTAL WATER RESEARCH PROJECT
A Public Agency for Environmental Research

Angela Licata
Deputy Commissioner for Sustainability
New York City Department of
Environmental Protection
59-17 Junction Blvd.
Flushing, NY 11373-5108

Re: Gowanus Canal Proposed Remedial Action Plan

Dear Ms. Licata:

I am writing in response to your inquiry regarding my 2006 study entitled "Watershed-Based Sources of Polycyclic Aromatic Hydrocarbons in Urban Stormwater" that was published in the journal *Environmental Toxicology and Chemistry*. I have attached a copy of that study, which deals with stormwater discharges in Southern California.

I am a Principal Scientist at the Southern California Coastal Water Research Project, a joint powers agency focusing on applied environmental research. My research focuses on effects of human activities on the condition of aquatic ecosystems, including research on multi-media distribution of environmental contaminants and stormwater assessment. A copy of my curriculum vitae is attached.

Per your request, I reviewed the Proposed Remedial Action Plan ("PRAP") for the Gowanus Canal Superfund Site ("Gowanus Canal"). On page 19 of the PRAP, EPA cites my 2006 study as follows:

> Scientific literature suggests that it can be assumed that the "first flush" comprises approximately 20% of the total discharge volume and contains between 30% and 60% of the total PAH load of the discharge (Stein, 2006).

As we discussed over the phone, extreme caution is necessary whenever research findings from one location and setting are generalized to apply to other areas. In this case, there are several factors that are different between Southern California coastal draining watersheds, where my study was conducted, and the locations applicable to the Gowanus Canal which have a direct bearing on conclusions about "first flush" and relative contaminant loading. First, my study pertains only to stormwater discharges, and not to discharges associated with CSOs. For stormwater in the Southern California study area ("study area"), all of the "first flush" releases directly to the receiving waterbody with no treatment. In contrast, the "first flush" for CSOs, or at least a significant portion of it, is designed to be captured and sent to a wastewater treatment plant before there is overflow to the waterbody. The treatment process has the potential to reduce the concentrations (and thus the loads) of particle-bound pollutants, such as PAHs.

Second, topographic and precipitation conditions—which have a significant effect on contaminant discharges—are much different in the study area from conditions in the area of the Gowanus Canal. Stormwater discharge of PAHs from urban watersheds is exacerbated in arid regions like Southern California. Specifically, long antecedent periods without rain (up to 142 days in Southern California) enhance the dry deposition of PAHs from atmospheric sources onto the land and subsequent washoff into the stormwater system. Conditions in the Gowanus Canal differ markedly, as the region is not arid and there are frequent rainfall events which may reduce the mass of material that accumulates on the land surface prior to being washed off during storms.

Third, the proportion of material that is found in the early portions of a storm, *i.e.*, the "first flush," depends in part on the velocity at which the stormwater is discharged. The relatively short, steep watersheds characteristic of Southern California result in high velocity discharges which are, in part, responsible for the proportionately higher concentration of PAHs in the "first flush." In contrast, the slope of CSO system into Gowanus Canal is relatively flat.

As with any research findings and accepted scientific methodology, the results from one situation should not be extrapolated or generalized to another unless they are first validated for the new situation. In other words, the general assumptions and patterns upon which our study was based should be tested and confirmed in the Gowanus Canal area in order to determine whether the conclusions in our study apply.

I hope this addresses your questions regarding the applicability of our research findings to the Gowanus Canal circumstances. Please feel free to contact me, or to have the EPA scientists contact me if you have further questions.

Sincerely,

Eric Stein

Eric D. Stein, D.Env.
Principal Scientist
Southern California Coastal Water Research Project