THE CHEMICALS

The CARP chemicals are polychlorinated biphenyls (PCBs), dioxins/furans, chlorinated pesticides, polynuclear aromatic hydrocarbons (PAHs), and the metals mercury and cadmium. Accessory parameters of particulate organic carbon (POC), dissolved organic carbon (DOC), and suspended sediment (SS) were also measured.

PCBs

PCBs and pesticides samples were usually acquired by TOPS. Extracts came from XAD resin and the glass fiber filters. On some occasions, samples were also taken from whole water grab samples, hexane (PISCES samples), sludges, and, for purposes of quality control, sediments. Details of the sampling procedures are to be found in the TOPS Standard Operating Procedure (SOP).

PCBs were measured by USEPA Method 1668A. The original Method 1668 was developed to measure the "co-planar" or "toxic" PCBs. At the outset of CARP one of the participating labs, Axys Analytical Services, suggested using an advanced version of 1668 called 1668A to measure all 209 PCB congeners. Methods 1668 and 1668A are descendents of 1613 in that they are isotopic dilution HRGC/HRMS methods. The modifications used were (a) using a single GC column (SPB-Octyl) which resulted in not all of the 209 congeners being resolved and (b) a 100 µL final extract volume which resulted in a 5-fold increase in the detection levels for each congener. The SPB-Octyl chromatographic column is short-lived and less familiar to many labs. This method was still experimental and has proved to be difficult for some of the labs to use.

Method 1668A does not resolve each of the 209 PCB congeners. During CARP Axys usually reported 159 domains consisting of from one (126 congeners) to 6 congeners or coelutions. Coeluted congeners are virtually identical. With two exceptions, each of the co-planar PCBs is resolved. The exceptions, IUPACs 156 and 157, have the same WHO98 TEF. Since these are HRMS data, all the coelutions have the same molecular weight. By convention, CARP reports all the coelutions under the name of the congener with the numerically lowest IUPAC designation.

PCBs can be treated as dioxins by summing the products of all congeners and their TEFs or they can summed to obtain a total PCB. The New York State Ambient Water Quality Standard (for protection of humans eating fish) sums all PCBs and is 1 pg/L. NYSDEC WQS do not recognize the co-planar PCBs. PCBs may have from one to 10 chlorine atoms. These result in one to 10 homologues. The relative abundances of the homologues can be useful in determining the source of the PCB.

PCBs were intentionally manufactured in the United States under the "Aroclor" trademark. Table 11 relates percent homologue abundance patterns to four Aroclors[4].

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[4] Shultz, D.E., Petrick, G., and Duniker, J.C. 1989. Complete characterization of polychlorinated biphenyls in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. ES&T 23, 852-859.

Table 12, also using data from Shultz et al, shows the percent abundances of congeners unique (some overlap, less than 10%, was permitted) to the lighter Aroclors (1016/1242) and heavier Aroclors (1254/1260). Typical Axys coelutions are indicated.

Table 11. Percent homologue abundances in four Aroclors.

Homologues	1016	1242	1254	1260
1-mono				
2-di	21.47	14.95		
3-tri	49.76	35.33	1.21	0.1
4-tetra	27.83	32.64	16.61	0.99
5-penta	0.99	13.16	50.96	13.51
6-Hexa	0.19	2.39	23.86	46.98
7-Hepta		0.22	4.38	33.83
8-Octa			0.68	7.27
9-Nona				0.67
10-Deca				0.05

Table 12. PCB congeners "uniquely" characteristic of Aroclors 1016/1242 ("Light") and 1254/1260 ("Heavy"). In percent abundance.

IUPAC	Group	1016	1242	1254	1260	Coelution	IUPAC	Group	1016	1242	1254	1260	Coelution
4	Light	3.89	3.01				131	Heavy			0.16	0.16	
5	Light	0.13	0.06				134	Heavy			0.49	0.62	143
6	Light	1.83	1.38				135	Heavy		0.08	1.62	2.56	151, 154
7	Light	0.6	0.6				136	Heavy		0.07	1.12	2.23	
8	Light	10.8	7.65				137	Heavy			0.25	0.06	
9	Light	0.95	0.54				138	Heavy	0.19	0.54	3.2	6.13	129
10	Light	0.37	0.2				141	Heavy			1.04	2.56	
15	Light	2.9	1.51				143	Heavy					134
16	Light	2.86	2.01				146	Heavy			0.83	1.49	
17	Light	3.84	2.88	0.19			147	Heavy					149
18	Light	9.03	6.28	0.41		30	151	Heavy			1.17	3.67	135
19	Light	0.96	0.53				153	Heavy		0.68	4.26	10.8	168
20	Light	1	0.29			28	154	Heavy					135
21	Light					33	156	Heavy		0.09	1.62	0.88	157
22	Light	4.8	3.41				157	Heavy				0.14	156
24	Light	0.3	0.22				158	Heavy			0.77	1.55	
25	Light	1.19	0.79				160	Heavy				0.05	129
26	Light	1.92	1.33			29	163	Heavy					129
27	Light	0.47	0.28				166	Heavy					128

Table 12 continued.

IUPAC	Group	1016	1242	1254	1260	Coelution	IUPAC	Group	1016	1242	1254	1260	Coelution
28	Light	8.71	6.52	0.25	0.05	20	167	Heavy			0.21	0.26	
29	Light	0.19	0.1			26	170	Heavy		0.11	0.31	3.91	
30	Light					18	171	Heavy		0.05	0.5	2.16	173
32	Light	1.34	0.88				172	Heavy			0.05	0.75	
33	Light	6.25	4.79	0.14		21	173	Heavy			0.09	0.36	171
34	Light	0.12	0.05				174	Heavy			0.34	3.85	
35	Light	0.08	0.11				175	Heavy			0.05	0.23	
37	Light	0.3	0.27				176	Heavy			0.32	0.95	
45	Light	1.66	1.16			51	177	Heavy			0.21	2.21	
46	Light	0.7	0.49				178	Heavy			1.35	1.62	
51	Light	0.36	0.23			45	179	Heavy			0.21	1.79	
59	Light	0.29	0.34			62, 75	180	Heavy		0.06	0.38	7.12	193
62	Light					59	183	Heavy			0.17	1.76	185
69	Light		0.11			49	185	Heavy				1.34	183
75	Light	0.08	0.11			59	187	Heavy			0.32	3.97	
122	Heavy			0.5	0.3		190	Heavy			0.08	0.79	
128	Heavy			2.07	1.06	166	193	Heavy				0.66	180
129	Heavy			0.23	1.11	138, 160, 163	201	Heavy			0.68	0.99	
130	Heavy			0.63	0.08								

Dioxins/Furans

Dioxins and furans were usually quantified only from suspended materials recovered by filters. Some XAD samples were analyzed for the dioxins but the margin between the detection limit and the amount recovered was usually uncomfortably small. There were also some whole water samples analyzed for the dioxins. Towards the end of the project a number of experiments were performed using metered surrogates of dioxins to examine the efficiency of XAD for these chemicals. Details of the sampling procedure for dioxins can be found in the TOPS SOP.

In the lab, the chlorinated dioxins and furans are measured using EPA Method 1613. This isotopic high-resolution gas chromatography/high resolution mass spectrometry procedure is well established and familiar to all the project labs.

Seven chlorinated dioxins and 10 chlorinated furans are considered. Each of these 17 chemicals is regarded as having a similar toxicological mode of action but also to have greatly differing potencies. These potencies are expressed as Toxic Equivalency Factors (TEFs). They also have differing potentials for bioaccumulation that are expressed as Bioaccumulation Equivalency Factors (BEF). The NYS Ambient Water Quality

Standard for the chlorinated dioxins and furans is the sum of the products of the observed concentrations and their TEFs and BEFs. The result is called the dioxin equivalents (TEQ). The NYSDEC Ambient Water Quality Standard (for protection of humans eating fish) for TEF, BEF chlorinated dioxins and furans is 0.6 femtograms/L (parts per quintillion).

Table 13. Dioxin/furan TEFs and BEFs

PARAMETER	WHO94	BEF
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	0.9
1,2,3,4,7,8-HxCDD	0.1	0.3
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.05
OCDD	0.001	0.01
2,3,7,8-TCDF	0.1	0.8
1,2,3,7,8-PeCDF	0.05	0.2
2,3,4,7,8-PeCDF	0.5	1.6
1,2,3,4,7,8-HxCDF	0.1	0.08
1,2,3,6,7,8-HxCDF	0.1	0.2
2,3,4,6,7,8-HxCDF	0.1	0.7
1,2,3,7,8,9-HxCDF	0.1	0.6
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.4
OCDF	0.001	0.02

Pesticides

Chlorinated pesticides were analyzed using a modification of USEPA Method 1613B. This is also a method high-resolution gas chromatography/high-resolution mass-spectrometry, combined with partial isotope dilution. A DB-5 column was used with a 200 µL final volume. Twenty-seven chlorinated pesticides were determined using 5 C-13 labeled and one deuterium labeled standards.

Table 14. CARP pesticides.

PARAMETER	WQS (ug/L)
2,4'-DDD	NA
2,4'-DDE	NA
2,4'-DDT	NA
4,4'-DDD	0.00008
4,4'-DDE	0.000007
4,4'-DDT	0.00001
Aldrin	0.001
HCH, alpha	0.002
HCH, beta	0.007
HCH, gamma	0.008
Chlordane,alpha (cis)	1
Chlordane,gamma (trans)	1
Chlordane,oxy-	NA
Heptachlor	0.0002
Hexachlorobenzene	0.00003
Mirex	0.000001
Nonachlor, cis-	NA
Nonachlor, trans-	NA
Dieldrin	6E-07
Endosulfan sulfate	NA
Endosulfan, alpha	0.001
Endosulfan, beta	0.001
Endrin	0.002
Endrin aldehyde	NA
Endrin ketone	NA
Heptachlor epoxide	0.0003
Methoxychlor	0.03

PAHs

PAHs were determined using high resolution gas chromatography with Selected Ion Monitoring low resolution mass spectrometry. A DB-5 column was used with a final volume of 500 µL.

The XAD resins used in TOPS release some of the PAHs targeted in the CARP. Therefore, dissolved phase PAHs were taken from the effluent of the TOPS cartridge filters. PAHs attached to particles were measured from glass fiber cartridge extracts.

The list of PAHs CARP uses includes a few where there are one or two methyl substitutions. These are called “C1” or “C2” as in “C1-Naphthalene”. PAHs can be summed but they may also be summed as a molar concentration. In this approach the individual chemical concentrations are divided by their molar weight and then added together.

Table 15. CARP PAHs.

PARAMETER	WQS (ug/L)	Molecular Wt.
1-Methylnaphthalene	NA	142.2
2-Methylnaphthalene	NA	142.2
Acenaphthene	6.6	154.2
Acenaphthylene	NA	152.2
Anthracene	NA	178.2
Benz[a]anthracene	NA	228.29
Benzo[a]pyrene	0.0006	252.3
Benzo[b/j/k]fluoranthenes	NA	252.3
Benzo[b]fluoranthene	NA	252.3
Benzo[e]pyrene	NA	228.3
Benzo[ghi]perylene	NA	228.3
Benzo[k]fluoranthene	NA	252.3
Biphenyl	NA	154.2
C1 Naphthalenes	NA	142.2
C1 Phenanthrenes/Anthracenes	NA	192.26
C2 Naphthalenes	NA	156.23
C3 Naphthalenes	NA	170.26
Chrysene	NA	228.3
Dibenz[a,h]anthracene	NA	278.4
Fluoranthene	NA	202.3
Fluorene	2.5	166.2
Indeno[1,2,3-cd]pyrene	NA	276.3
Naphthalene	16	128.2
Perylene	NA	252.32
Phenanthrene	1.5	178.2
Pyrene	NA	202

Metals

Field contamination has posed a substantial problem in sampling trace levels of metals, particularly mercury. Overcoming this problem requires a great deal of vigilance and the procedure has been formalized into an act of ritual cleanliness called “Clean Hands/Dirty Hands”. It’s also called USEPA Method 1669. Early in the life of the project we brought Michelle Gauthier from Frontier Geosciences in Seattle, WA to help us with the sampling technique. We took her out on the East River and to the Newtown Creek WPCF to see two typical and different sampling environments.

Details of the procedure to avoid contaminating the sample in the field are given in the TOPS SOP. Essentially, one person handles the placement of water into the bottles and a second helper opens Ziploc bags holding the sampling equipment while a third takes field notes. Filtration for dissolved metals is performed in the field.

During trackdown, metals were collected by duct taping a clean sample bottle to a weighted line, submersing the bottle, capping it immediately on recovery, and re-double bagging it.

All metals sample processing took place using ultra-clean handling techniques in a class 100 clean area known to be low in atmospheric mercury. Reagents, gases, and reagent water were all reagent or ultra-pure grade and previously analyzed for trace metals to ensure very low blanks.

Water samples were prepared according to Frontier Geosciences SOP #FGS-032. Metals (Ag, Cd, and Pb) preserved to pH 1.8 with HNO_3 are extracted with Co-APDC, and the precipitate is collected by filtration. The precipitate is then dissolved in concentrated HNO_3 , then diluted in 5% HNO_3 to 10 mL. This method allows for the removal of the analytes of interest from the sample matrix, and makes possible up to 20-fold concentration of the sample.

Silver, cadmium, and lead were determined using inductively coupled-mass spectrometry (ICP-MS, US EPA Method 1640, modified) with a Perkin-Elmer Elan 6000. All results are reported instrument and preparation blank corrected.

Mercury analyses were performed using cold vapor atomic fluorescence spectrometry (CV-AFS). Total mercury standards are prepared by direct dilution of NIST-certified NBS-3133 mercury standard solution and results are independently verified by analysis of NIST 1641d. For the digestion/oxidation of water samples, BrCl was added to an aliquot of the sample at a level of 1-5 mL/ 100 mL of sample depending on apparent level of organics and turbidity of the samples. Sample oxidation took place on the same day of sample receipt. Samples were allowed to digest overnight at room temperature. Digests were analyzed for total Hg by CV-AFS. Aliquots of each digest were reduced in pre-purged reagent water to Hg° with $SnCl_2$ and then the Hg° purged onto gold traps as a preconcentration step. The Hg contained ion the gold traps was then analyzed by thermal desorption into an atomic fluorescence detector using the dual amalgamation technique.

For methyl mercury analysis water samples were distilled to liberated MeHg (US EPA Draft Method 1630). For water samples, 45 mL of 0.4% (v/v) HCl acidified sample was distilled using 50 mL Teflon distillation tubes. To each sample, 0.2 mL of 1% APDC solution was added prior to distillation, to enhance reproducibility and recovery. The distillate was received into a tube containing 5.0 mL of DDW to start, and distilled to 40.0 mL. Thus 35 mL out of 45 mL of sample was distilled over for analysis. The historic mean MeHg distillation recovery is 90.6 %. All net MeHg results are corrected for this efficiency factor.

Distilled samples were analyzed using aqueous phase ethylation, purging onto a Carbotrap, isothermal GC separation, and CV-AFS detection. Prior to ethylation, the distillate was diluted to 55 mL with DIW, and the pH brought to 4.9 with acetate buffer. Samples were ethylated by the addition of sodium tetraethyl borate, and then the volatile ethyl analogs purged with N_2 onto Carbotrap.After a trap drying step, the mercury ethyl

analogs were thermally desorbed into a 1 m isothermal GC column (15% OV-3 on Chromosorb WAW-DMSC) held at 100°C for separation. The column resolves elemental Hg, dimethyl Hg, methyl ethyl Hg, and diethyl Hg. Only methyl ethyl Hg, the MgHg analog, is quantified. The organo-Hg compounds are pyrolytically decomposed to Hg° prior to entering the CV-AFS detector.

Water quality standards for the metals appear in Table 16.

Table 16. Water Quality Standards for metals.

	ng/L	Water Class	Type	form
Cadmium	7,700	SA, SB, SC, I	A(C)	
Lead	8,000	SA, SB, SC, I	A(C)	
Mercury	0.7	SA, SB, SC, I, SD	H(FC)	dissolved
Silver	100	A, A-S, AA, AA-S, B, C	A(C)	ionic

SS/DOC/POC

Suspended solids (SS) measures the total amount of particulate material suspended in the water column. At the beginning of the project we collected bottles of water that would be passed through pre-weighed filter paper, dried, and re-weighed. Some of the sites had very low suspended solids concentrations resulting in non-detections. We changed the procedure and brought pre-weighed filters and filtration equipment into the field where sufficient water was passed through the filters to obtain noticeable plugging. Particulate Organic Carbon (POC) sampling was similar. For POC, we tried to collect and filter water continuously over the span of time that TOPS was operated. Both SS and POC samples were kept frozen before being sent for analysis. The POC filters were also cored. David Hirschberg, the POC/DOC expert at SUNY Stony Brook, asked us to send him 10 mm disks. Initially, we sent him one 10 mm disk for each sample but later we sent three. This was due to apparent inhomogeneity of deposition on the filters. Dissolved organic carbon (DOC) was field filtered and acidified. Details of all three procedures appear in the TOPS SOP.

POC was measured on a Carlo Erba EA1108 CNS Analyzer. DOC was quantitated on Shimadzu TOC-5000, a high temperature oxidation type instrument. POC accuracy was assessed through use of a variety of internal and NIST standard reference materials. DOC analyses are intercalibrated through the use of internationally distributed intercalibration materials supplied by Dr. Jon Sharp at the University of Delaware and supported by the National Science Foundation.

Determination of suspended sediments, POC, and DOC at the USGS stations was more complicated. Large numbers of samples were taken across a changing hydrograph. These observations were combined to yield loads. We took the loads and back-calculated concentrations. The methods for combining the observations are described in Potterfield

(1972) - Techniques of Water Resources Investigations (TWRI) of the United States Geological Survey, Book 3, Chapter C3 - Computation of Fluvial-Sediment Discharge. The TWRIs are a series of "How To" publications the USGS puts out on a wide variety of things done on a regular basis. All survey offices computing suspended sediment loads use the same method - how they perform the computation (by hand, spreadsheet, USGS daily loads software, etc.) may vary based on the available data set.

Steps for calculating suspended sediment loads:

1 - Compile the discharge data
- 1a) review and correct daily values
- 1b) determine which 15 minute and hourly raw values are good/bad (USGS doesn't correct raw 15 min data, only the daily data).

2 - Compile the concentration data
- 2a) review QC samples
- 2b) track down missing data and any discrepancies.

3 - Determine a "box coefficient"
- 3a) plot equal width vs. point samples
- 3b) determine if coefficient is flow or seasonally dependent - other factors are possible.

4 - Apply the coefficient to the data.

5 - Generate a plot of concentration vs. discharge (and/or other parameters) for possible use in estimating periods with no record.

6 - Plot the adjusted data on a trace of stage and/or discharge.

7 - Generate a continuous concentration curve - this involves some art and a feel for how the constituent behaves at the site, it's basically an educated guess as to what the concentration was between samples. Obviously, the quality of the curve is highly dependant on the sample frequency - during TOPS event we were collecting a lot of samples, so the quality of the concentration curve is pretty good during these periods.

8 - Determine if the day should be "subdivided" - i.e. if the concentration curve and or the discharge changes dramatically over the course of the day ("dramatically" is more clearly defined in Potterfield (1972),
- 8a) subdivision involves segmenting the day into smaller, more uniform parts, computing the load for those periods, and summing the periods for the day,
- 8b) if required, the day was broken down into hour segments and the"mid-interval" method described by Potterfield (1972) was used.

9 - If the day doesn't need to be subdivided, determine the average concentration for the day from the continuous concentration curve.

For POC and DOC many of the same steps used in the sediment computation apply - here are some of the highlights:

POC

1 - Apply sediment box coefficient to POC data.

2 - For all 3 sites, reasonable relations exist between POC and suspended sediment these

are used to help estimate POC concentrations during periods with no data.
3 - Plot adjusted POC, model POC, and anything else that might help determine the continuous concentration curve on a trace of discharge and or stage.
4 - Computations are identical to sediment - including subdividing days.

DOC
1 - The variability of DOC between samples is generally small, so linear interpolation between samples (computation of a noon value) was used to estimate many of the daily values.
2 - Plot DOC, model DOC (interpolated values), and anything else that might help determine the continuous concentration curve on a trace of discharge and or stage; 2a - if the model wasn't responding to the discharge (for example – samples bracketing a discharge event) the concentration curve was adjusted by hand based on knowledge of how the constituent behaves at the site.
3 - Subdivision was rarely necessary because of the low variability in DOC concentrations, otherwise the computations were identical to POC and sediment.

QUALITY CONTROL

Data generated by the CARP are initially loaded into a data management system operated by Battelle Ocean Sciences of Duxbury, MA under the direction of Tom Gulbransen. Battelle screens incoming data for conformity to the rules of the Electronic Data Deliverable and admits those that are properly formatted. A second step of validation is being performed by Booze Allan Hamilton, a contractor to the Hudson River Foundation. The validation will consist of passing all data through a screen to determine compliance with certain QC parameters. At this time, none of the data have been "validated". "Validated" data will supplant unvalidated data. NYSDEC does not normally used third part validation for its regulatory or enforcement work.

The amount of data collected by CARP is enormous; the water portion alone has produced a quarter of a million records. Many interested users will want to ask questions of the data that we have not anticipated. Others may want to have a simpler contact with the project and will be satisfied to have us paint a broad picture of the findings. The first group of users will go to our website (www.carpweb.org). This site includes maps, a variety of data screens, and a metadata document that explains the structure of the database.

Quality Control – Field QC

Previous experience has indicated that there may be significant lab to lab differences in measurement of trace organic chemicals. In CARP, three organics laboratories produced data for the NYSDEC water program. In order to determine the degree of inter-laboratory variability, a 5-gallon sediment sample was taken from the Arthur Kill near the northern side of Pralls Island at the beginning of the project. This material was

thoroughly homogenized and divided into vials that were kept frozen. From time to time, these vials were sent in to the labs and analyzed for the suite of CARP substances. Ultimately, Axys (AAS) received 26, Severn Trent (QTS) saw 10, and Wright State University (WSU) got 4. Each lab should have been receiving essentially the same material and should have been producing the same results. The actual results (average/standard deviation) are indicated below graphically (Figures 16-21).

Table 17. Interlab variability, Pralls Island sediments.

	AAS	QTS	WSU
Dieldrin, ug/kg	5/1.3	2.3/1.1	10/4.4
Dioxin/Furans, ug/kg TEQ	0.18/0.076	0.05/0.014	0.14/0.12
PAH, umoles/kg	91/28	24/2.8	55/48
PCB, ug/kg	1700/380	880/94	1100/160
Total Chlordane, ug/kg	31/9	10/4.4	50/46
Total DDT, ug/kg	980/400	840/1200	1000/340

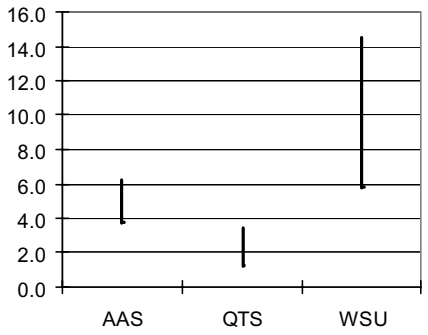

Figure 16. Field QC comparisons, Dieldrin in ug/kg. Mean +/- one standard deviation.

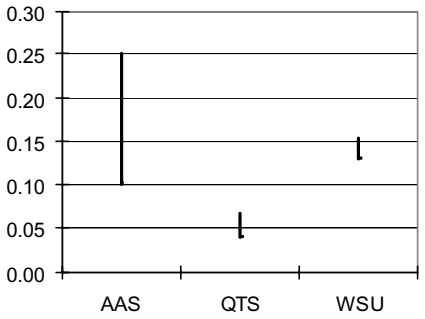

Figure 17. Field QC comparisons, TEQ dioxin/furan in ng/kg, mean +/- one standard deviation.

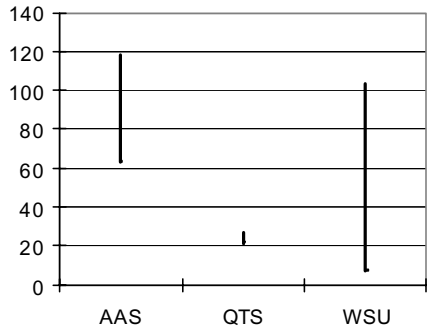

Figure 18. Field QC comparisons, PAHs in umoles/kg. Mean +/- one standard deviation.

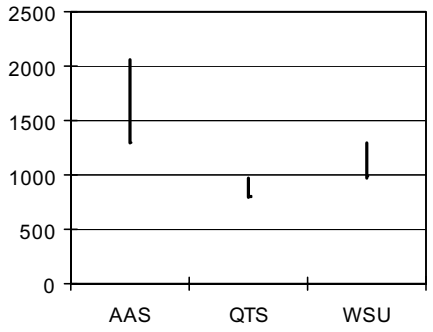

Figure 19. Field QC comparisons, PCBs in ug/kg. Mean +/- one standard deviation.

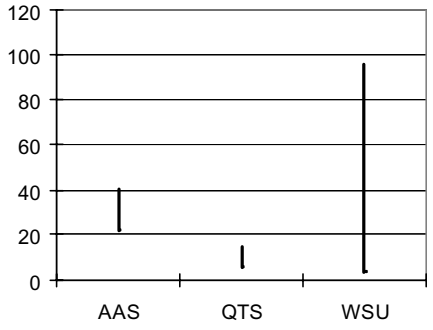

Figure 20. Field QC comparisons. Total chlordane in ug/kg. Mean +/- one standard deviation.

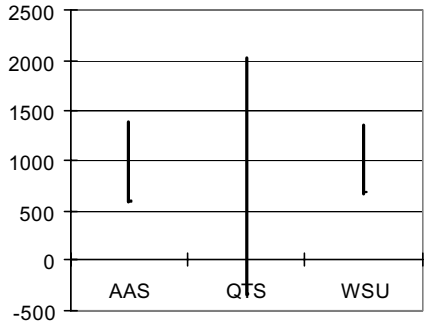

Figure 21. Field QC comparisons. Total DDT in ug/kg. Mean +/- one standard deviation.

Quality Control – Field Blanks and Equipment Blanks

A variety of experiments were performed to assess inadvertent contamination of the samples. The experiments fall into two broad groups, Field Blanks (FB) and Equipment Blanks (EB). FB are samples of media, glass fiber filters or XAD columns that are brought into the field unused, and returned to the lab. EB are samples of filters, XAD, or water that had been run through TOPS after routine cleaning.

The results of the blank experiments should be compared with the samples on the basis of total mass of recovered analyte rather than concentration.

1) unfired filter
2) processed after lower East River cruise
3) 96 L of Colonie, New York tap water transported to a sampling site on Staten Island and back to Colonie, New York and then processed via TOPS-Next Generation.

The significance of the field and equipment blank values is in how they measure against actual sample observations. The relevant units from the blanks are mass, not concentration. Therefore, the comparison with the sample observations must be the mass of analyte recovered from the medium.

Table 18 summarizes the results of field and equipment blanks.Table 18. Field and equipment blanks.

Samp ID	Field Code	Lab ID	Medium	dieldrin ng	diox-F pg TEQ	PAH nmoles	PCB ng	T Chlor. ng	TDDT ng
1SPL00015	FB	AAS	filt. Water			0.1			
1SPL00521	FB	AAS	glass fiber cart.	<0.32	1.57	1.4	1.3	0.2	0.24
1SPL00588	FB	AAS	reagent water			0.24			
1SPL00595	FB	AAS	glass fiber cart.	<0.37	2.1	0.75	2.6	<3.8	<11
1SPL00596	FB	AAS	XAD	<0.59	1.6		25	<4.5	<14
1SPL00944	FB	AAS	XAD	<0.82		0.12	3.7	<3.4	<3.6
1SPL01625 [1]	FB	AAS	glass fiber cart.	0.13	11	72	74	0.91	0.27
1SPL01780	FB	AAS	XAD	<0.22			1.4	<0.41	0.48
1SPL01781	FB	AAS	glass fiber cart.	<0.096	8	1	1.5	<0.35	<1.7
1SPL01814	FB	AAS	glass fiber cart.	<0.077	7	0.67	8.3	<0.26	<1.2
1SPL01815	FB	AAS	XAD	<0.15			1.6	0.38	3.4
1SPL01858	FB	AAS	XAD	<0.083			0.83	0.33	<6.1
1SPL01859	FB	AAS	glass fiber cart.	<0.16	0.24		0.31	<0.76	<4.8
1SPL01896	EB	AAS	filt. water (AE,GF/F)		0.3		0.17		
1SPL01897	EB	AAS	filt. AE+GF/F				0.58		
1SPL02123	FB	WSU	XAD	<4.6			6.4	<12	<6.2
1SPL02124	FB	WSU	glass fiber cart.	<2.7	7.1	3.6	15	<11	280
1SPL02145 [2]	FB	WSU	glass fiber cart.	<3.1		2.6	15	<16	15
1SPL02159 [2]	FB	WSU	XAD	<3.1			11	<8.3	<5.4

Table 18 continued.

Samp_ID	Field Code	Lab_ID	Medium	Dieldrin ng	Diox-F pg TEQ	PAH nmoles	PCB ng	T Chlor. ng	TDDT ng
1SPL02182	EB	WSU	filt. water (AE,GF/F)			0.48			
1SPL02183	EB	WSU	filt. water (AE,GF/F)			0.34			
1SPL02193	EB	WSU	filt. water (AE,GF/F)			0.42			
1SPL02194	EB	WSU	filt. water (AE,GF/F)			0.47			
1SPL02210	EB	WSU	XAD	<1.6			13	<10	<5.1
1SPL02212	EB	WSU	glass fiber cart.	<5.3	28	5.9	11	<21	<6.1
1SPL02285	EB	WSU	filt. water (AE,GF/F)			0.87			
1SPL02294	EB	WSU	filt. water (AE,GF/F)			1.3			
1SPL02295	EB	WSU	filt. water (AE,GF/F)			1.3			
1SPL02309	EB	WSU	glass fiber cart.	<3.5	0.26	5.7	13	<15	<7.8
1SPL02310	EB	WSU	XAD	<2.5			9.1	<17	<6.8
1SPL02317	EB	WSU	filt. water (AE,GF/F)			0.26			
1SPL02318	EB	WSU	filt. water (AE,GF/F)			0.19			
1SPL02373	EB	AAS	filt. water, Post XAD	<0.0045	1.5	1.2	11	<0.031	<180
1SPL02374	EB	AAS	XAD	0.036			4.8	0.062	<1.5
1SPL02375	EB	AAS	glass fiber cart.	0.046	1.7	0.79	1.4	<0.37	<2.2
1SPL02577	FB	AAS	glass fiber cart.	<0.030	2.9	1.4	0.78	<0.41	<3.1
1SPL02578	FB	AAS	XAD	<0.019			0.8		
1SPL02621	FB	AAS	XAD	<0.0041			1.6	<1.1	<2.7
1SPL02622	FB	AAS	glass fiber cart.	<0.057	4	1.3	0.8	<0.34	<2.6
1SPL02820 [3]	EB	AAS	XAD	<0.056			5.6		
1SPL02821 [3]	EB	AAS	XAD	2.6			68		
1SPL02873 [3]	EB	AAS	glass fiber cart.	<0.086			0.67		
1SPL02953	EB	AAS	reagent water		12		1.2		
1SPL03012	EB	AAS	XAD	<0.32	5.6		48	<2.3	<7.9
1SPL03013	EB	AAS	glass fiber cart.	<0.19	7.3	6.7	1.4	<2.1	<8.1

PCB Blanks

In the case of PCBs, the highest blank value for XAD was 68 ng. The lowest sample mass from either a primary XAD column (first in the series) or a combined XAD (both columns extracted and analyzed together) was 80 ng and the 1th percentile (99 percent of observations were greater) was 100 ng. That 68 ng blank was from a sample of 96 L of tap water that had been put in large glass carboys, driven to Staten Island and back, and then processed in the lab. Had it been treated as a sample, the resultant concentration would have been 0.7 ng/L. The blank XAD with the next lowest PCB mass came from a

column with visible discoloration and had last been used to process landfill leachate. The homologue distribution of that blank does not look like a commercial PCB.

The highest levels of PCB found in a filter cartridge (74 ng) occurred from one that had not been fired in a furnace for 4 hours at 450?C. All glass fiber filter media used in the project for samples had been fired. The next highest blank filter PCB value was 15 ng. This value does begin to impinge on the data.

Dioxin/Furan Blanks

Dioxins/furans were measured mostly from glass fiber cartridges. The maximum blank was 28 pg TEQ and the next highest value (11 pg TEQ) was from the unfired filter. The average glass fiber filter blank was 6.2 pg TEQ. These blanks impinge on sample data; the 25th percentile for glass fiber cartridges was 23 pg TEQ and the 10th percentile was 10 pg TEQ.

Data from 99 dioxin/furan analyses on XADs (first or combined) had a median value of 3.4 pg. The blanks had a mean of 3.6 pg TEQ.

PAH Blanks

The average blank for PAHs from cartridges expressed as summation of moles, (ignoring the unfiltered cartridge with its 72 nmoles) was 2.7 nmoles. This is compared against the 5th percentile value for samples of 6.9 nmoles. The maximum cartridge blank contamination level was 6.7 nmoles.

The average blank value for water analyzed for PAHs was 0.63 nmoles. The 30th percentile value for the filtered water samples was 0.6 nmoles. Dissolved PAHs had no field concentration due to the potential of contamination by XAD resin.

Total DDT Blanks

Total DDT (2,4'-DDT, DDD, and DDE and 4,4'-DDT, DDD, and DDE) samples were much like the PCBs where they were measured from cartridges and XAD. Ten cartridge blanks had total DDT masses below the detection limit (max detection limit was 8.1 ng). Four samples had quantifiable TDDTs and ranged from 280 to 0.24 ng. The 1th percentile TDDT mass in the samples was 3.6 ng. There is no ready explanation for the very high blank (280 ng); the next highest, 15 ng, was from the unbaked filter. It is possible that the large value was a decimal error but there were values for five of the six analytes.

The 5th percentile of the first and combined XAD columns for TDDT was 2.8 ng. Ten XAD blanks were non-detect and two were quantitated values of 3.4 and 0.48 ng.

Dieldrin Blanks

Dieldrin was non-detect on 13 blank cartridges and detected twice at 0.046 and 0.13 ng. The 1th percentile for dieldrin on samples was 0.37 ng.

Blanks for dieldrin were non-detect from 13 XADs and quantitated on two at 0.036 and 2.6 ng. Of the first and combined sample XAD columns, the 5th percentile was 4.6 ng.

Total Chlordane Blanks

Total chlordane (alpha-, trans, and oxy-chlordane) had non-detect blanks on 12 cartridges and detected values in two of 0.2 and 0.91 ng. The 5th percentile for total chlordane on cartridges was 2.3 ng.

Nine XAD blanks had no measurable chlordane. Three had values ranging from 0.38 to 0.062 ng. The 1th percentile for total chlordane in first or combined sample XADs was 0.77 ng.