UNITED STATES ENVIRONMENTAL PROTECTION AGENCY - REGION III
OFFICE OF ANALYTICAL SERVICES AND QUALITY ASSURANCE
Environmental Science Center
701 Mapes Road
Fort Meade, Maryland 20755-5350

DATE: October 17, 2007

SUBJECT: DRBC Ambient Water Monitoring of the Delaware River for Emerging Contaminants Quality Assurance Project Plan (QA Document 28002)

FROM: Mary Ellen Schultz, Environmental Scientist *mes*
OASQA/Technical Services Branch (3EA22)

TO: Patricia Iraci, Project Officer
Water Protection Division (3WP00)

The Ambient Water Monitoring of the Delaware River for Emerging Contaminants Quality Assurance Project Plan (QAPP), which was revised per comments in my July 27, 2007-memo, has been reviewed. All comments have been adequately addressed. Therefore, I recommend approving the QAPP.

If you have any questions, please contact me at (410) 305-2746.

AMBIENT WATER MONITORING OF THE DELAWARE RIVER FOR EMERGING CONTAMINANTS

QUALITY ASSURANCE PROJECT PLAN

Date: October 1, 2007

DELAWARE RIVER BASIN COMMISSION

DRBC Project Officer	A. Ronald MacGillivray, Ph.D.	date
DRBC Quality Assurance Officer:	Edward D. Santoro, M.S.	date
USEPA Project Officer	Patricia Iraci	date
USEPA Quality Assurance Officer		date

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2. PROJECT MANAGEMENT ELEMENTS

The elements in this section address project management, including project background and objectives, roles and responsibilities of the participants. These elements document that the project has a defined goal and the approach to be used, and that the outputs have been documented.

2.1 Distribution List

Signed copies of this Quality Assurance Project Plan (QAPP) and all subsequent revisions will be sent to the following individuals by electronic mail**:**

Distribution List

Individual	Organization
Dr. Thomas Fikslin	Delaware River Basin Commission
Mr. Edward D. Santoro	Delaware River Basin Commission
Dr. A. Ronald MacGillivray	Delaware River Basin Commission
Ms. Carol Collier	Delaware River Basin Commission
Ms. Patricia Iraci	U.S. EPA, Region III
Toxics Advisory Committee Members & Alternates	

Printed copies will be available upon request. Furthermore, copies of this QAPP and all subsequent revisions will be available from the Delaware River Basin Commission (DRBC) web site at http://www.state.nj.us/drbc/

2.2 Project / Task Organization

Figure 1 below identifies the individuals and organizations participating in the project and outlines the formal lines of responsibility.

Figure 1, Lines of Responsibility

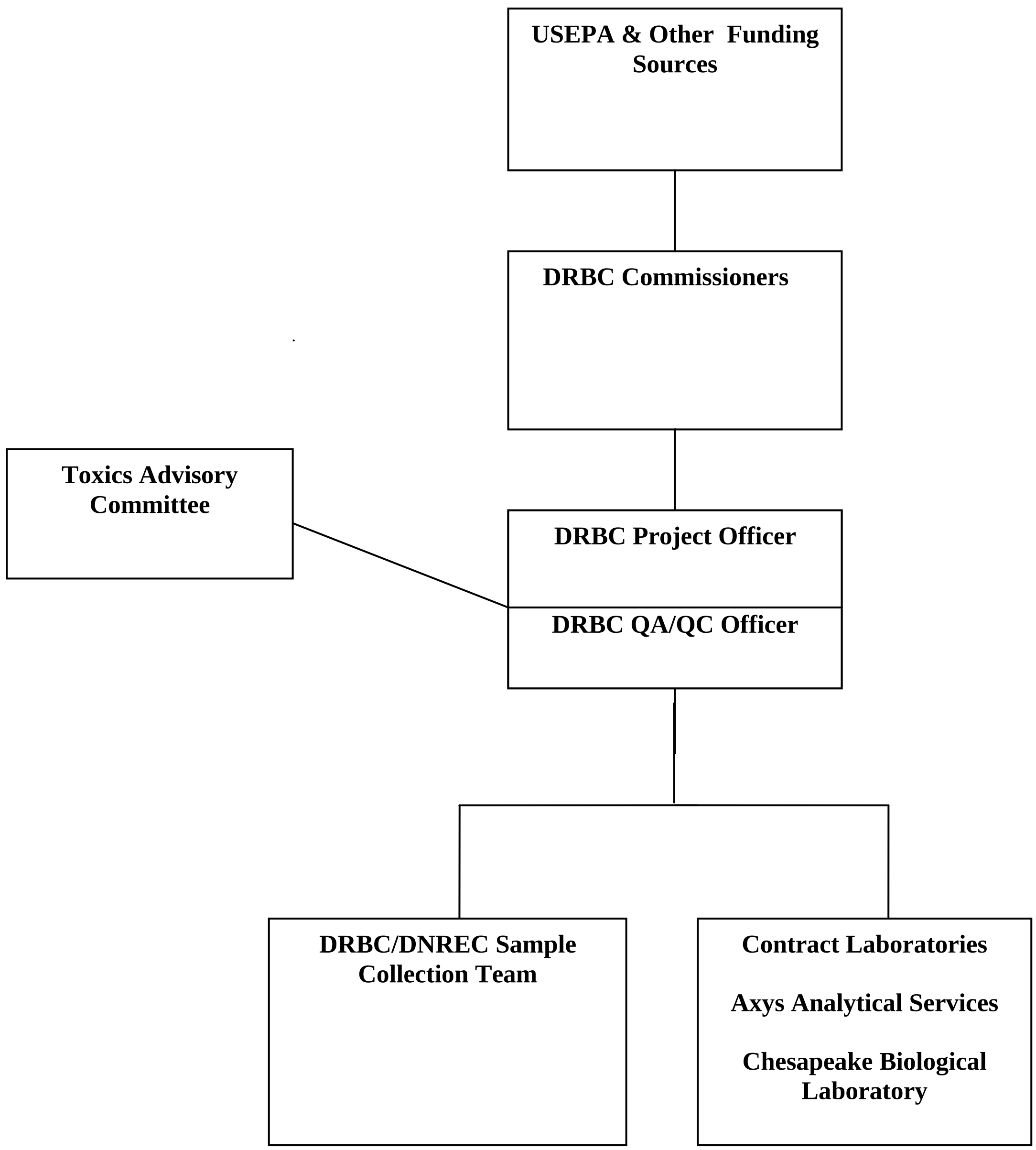


Table 1 Roles and Responsibilities of Key Project Individuals

Key Individual	Title	Phone	Responsibility
Thomas Fikslin, Ph.D. DRBC	Branch Head	(609) 883-9500 x253	General oversight of program. Technical support. Contract Officer.
Laurie Phillips	Laboratory Manager Axys Analytical Services	(250)655-5800	Ensure that all analytical QA/QC requirements are met and analytical data package is transmitted to DRBC for emerging contaminant parameters.
Edward D. Santoro, M.S. DRBC	DRBC QA/QC Officer	(609)883-9500 x268	Ensure that the overall quality assurance of the project is achieved. Ensures that activities are coordinated between DRBC, DNREC, and analytical laboratories to meet project schedule.
A. Ronald MacGillivray, Ph.D. DRBC	DRBC Project Officer	(609)883-9500 x252	Provide overall project coordination, including the preparation of a quality assurance project plan, the scheduling of project tasks to ensure timely completion, coordination and oversight of sampling, the review of the data to determine compliance with QA/QC requirements and the overall quality of the data. Oversee collection of water samples.
Carl Zimmerman	Laboratory Manager Chesapeake Biological Laboratory (CBL) Nutrient Analytical Services	(410)326-7302	Ensure that sample container preparation and analysis of samples for organic carbon specified in the project plan are coordinated with DRBC. Ensure that all QA/QC requirements are met for test parameters; and data package is transmitted to DRBC.

2.3 Problem Definition and Background

There are more than 85,000 chemicals commercially available in the United States with new chemicals and technologies introduced each year. The number of substances released to the environment, improved analytical methods and a growing body of information on adverse effects has increased interest by scientists, the public and regulators in substances and toxic effects not historically monitored or assessed. These emerging contaminants of concern (ECOC) are substances that have been detected in humans or other living organisms, have been found to be toxic in some way, or are persistent in the environment. Therefore, the substance may have the potential to cause adverse effects on human health or the environment. Examples of ECOC include phthalates, perchlorate, brominated flame retardants, nanoparticles, pharmaceuticals and personal care products. A number of efforts are underway within the Delaware River Basin to identify, understand and prioritize ECOC. Studies sponsored by the United States Environmental Protection Agency (USEPA), United States Geological Survey (USGS), basin states and private industry have generated and continue to generate data on ECOC from locations within the Delaware River Basin. In 2006, the Delaware River Basin Commission (DRBC) included a select number of ECOCs in ongoing fish tissue monitoring.

The DRBC monitoring schedule in 2004, 2005, 2006 includes fish tissue analysis of polybrominated diphenyl ethers (PBDE) and perfluorooctanoic acids (PFOA) along with dioxins/furans, PCB, chlorinated pesticides and metals.

A list of target ECOC for ambient water monitoring in the mainstem of the Delaware River by the DRBC is included in this screening survey. The compounds listed have published analytical methods for detection in surface water therefore eliminating the need for time consuming and expensive method development. Most of the compounds are USGS surface water target compounds and have been detected in the Delaware River Basin. The list also includes the pharmaceutical carbamazepine because it has been detected in sewerage treatment plant discharges and has been identified through risk assessment to be a high risk in aquatic environments. PBDE and PFOA compounds are included in the DRBC list because they have been detected in Delaware River Basin fish tissue.

2.4 Project / Task Description

Samples will be collected on one sample day from the center channel in the mainstem of the Delaware River. The 16 sample site locations in the tidal river are the same sites to be sampled in the DRBC Ambient Water Monitoring of the Delaware River for Chronic Toxicity. When practical, samples will be taken concurrently to conserve resources. The ambient whole water samples will range in salinity from brackish (15 ppt) to freshwater (<1 ppt). In-field testing at all sites on each sample day for specific conductivity, salinity, water temperature, dissolved oxygen and pH will be conducted. Laboratory analysis will be conducted for alkalinity, chloride, hardness (freshwater samples only), and the DRBC Target List for Emerging Contaminants.

2.5 Quality Objectives and Criteria

Quality Assurance consists of activities to ensure that data meet the quality needed. Quality assurance practices such as: (1) sampling and handling; (2) condition of equipment; (4) test conditions; (5) instrument calibration; (6) replication; (7) record keeping; and (9) data evaluation.

This section describes methods used to determine the precision, accuracy, representativeness, and completeness of data generated.

2.5.1 Precision

For field measurements, precision of water quality parameter measurements will be determined by relative percent difference (RPD) of duplicate measurements. Measurements will be taken at the beginning and end of each series of sample measurements. If the RPD exceeds 10%, corrective action will be taken.

$$RPD = [(C_1 - C_2)/\{ (C_1 + C_2)/2)\}] X100$$

RPD = Relative Percent Difference
C_1 = Larger of two observed values
C_2 = Smaller of two observed values

2.5.2 Accuracy

Accuracy of water quality parameter measurements will be determined by comparing the measured value of a standard against the known value of the standard. Accuracy will be expressed in terms of the relative error as the percent deviation of the measured value from the known value or relative percent difference. If the relative percent difference (RPD) exceed 10%, corrective action will be taken.

$$RPD = [(C_1 - C_2)/\{ (C_1 + C_2)/2)\}] X100$$

RPD = Relative Percent Difference
C_1 = Larger of two observed values
C_2 = Smaller of two observed values

2.5.3 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the sampling and analysis plan is followed and that proper sampling techniques are used. Representativeness in the laboratory is ensured by using the proper procedures, meeting sample holding times and analyzing and assessing controls.

2.5.4 Completeness

It is anticipated that all samples received by the laboratory will be tested and that the criteria for test acceptability for each test method will be met**.** Following completion of the toxicity testing, the percent completeness will be calculated.

$$Completeness = \frac{V}{P} \times 100$$

Where:
V = Number of valid tests
P = Number of planned tests

2.6 Analysis of Physical-Chemical Parameters

Chemical and physical analysis of the ambient river water must include established quality assurance practices outlined in the methods listed.

2.7 Calibration and Standardization

Instruments used for measurements of chemical and physical parameters such as pH, DO, temperature, and conductivity must be calibrated and standardized each day before use according to instrument manufacturer's procedures. Calibration checks will be done during the sampling day. Calibration data will be documented.

All other instrument and equipment calibration requirements are associated with the contract laboratories. Laboratory instrument and equipment calibration requirements are described in the methods listed.

2.8 Training, Sampling, and Laboratory Procedures

Sample collection will be conducted by individuals who are knowledgeable in sampling procedure. Prior to sampling, all members of the sampling team will review the QAPP and DRBC staff will have read the DRBC's "Field Safety Manual". Laboratory managers will be familiar with applicable sections of the QAPP. Laboratory staff will be familiar with protocols and SOPs associated with each laboratory test method.

2.9 Chain of Custody

The sample collection team is responsible for the care and custody of the samples until they are transferred to the laboratory. As few people as possible should handle the samples. The sample collection team must complete a chain of custody form documenting the custody of each sample following sample collection. The sample numbers, locations, date and time will be listed on the chain of custody form. This chain of custody will follow the samples as they progress through collection and testing. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to a laboratory, or to/from secure storage.

2.10 Documentation

A laboratory report will be submitted to the DRBC in electronic format and as hard copy. The report will include a description of all statistical analysis and raw data. The DRBC Project Officer will be responsible for maintaining on file at the DRBC all documents and records associated with this project.

3. DATA GENERATION AND ACQUISITION

3.1 Physical-chemical analysis of ambient water

The physical-chemical parameters of ambient waters is listed in Table 2. In-field testing at all sites of specific conductivity, salinity, water temperature, dissolved oxygen and pH will be conducted.

Laboratory analysis will be conducted according to the methods listed in Table 3 for alkalinity and chloride, (physical-chemical parameters with holding times $\leq$28 days) and hardness (freshwater sites only).

Mainstem site transect composites will be analyzed for the contaminants listed in Table 4.

All methods can be replaced with an equivalent method after consultation with the DRBC.

Table 2: Physical-Chemical Parameters of Ambient Water Measured In-Field

Parameter	Meter	Unit	Method	Number of In-Field Samples
SPECIFIC CONDUCTIVITY	Hydrolab or YSI	µS/cm	International Organization of Standardization 7888-1985 or Standard Method 2510	17
SALINITY	Hydrolab or YSI	ppt	Standard Method 2520	17
WATER TEMPERATURE	Hydrolab,YSI, or Mercury Thermomter	^{o}C	Standard Method 2550 Thermometric	17
DISSOLVED OXYGEN	Hydrolab, YSI or Corning	ppm or % saturation	Standard Method 4500 O-Membrane Electrode	17
pH	Isfet or equivalent	Standards units	Standard Method 4500 H+ Electrometric	17

Table 3: Methods of Analysis for Physical-Chemical Parameters of Ambient Water Collected

Parameter	Method	Container	Holding Time	Preservation Requirement	Laboratory
ALKALINITY	APHA Method 2320	HDPE	24 hours	None required	CBL
CHLORIDE	EPA 300.0	100 ml HDPE	28 days	None required	CBL
HARDNESS (FRESHWATER SITES ONLY)	APHA Method 2340 B or C	125 ml HDPE	6 months	HNO_3 to pH <2 Cool, $4^{0}C$	CBL

Table 4: Analytical Methods for DRBC Emerging Contaminants List

Parameter	LOQ	MDL	units	Method	Laboratory
2,2',3,4,4',5',6-HeptaBDE (BDE-183)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',3,4,4',5'-HexaBDE (BDE-138)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',3,4,4'-PentaBDE (BDE-85)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',4,4',5,5'-HexaBDE (BDE-153)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',4,4',5,6'-HexaBDE (BDE-154)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',4,4',5-PentaBDE (BDE-99)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',4,4',6-PentaBDE (BDE-100)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',4,4'-TetraBDE (BDE-47)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,2',4-TriBDE (BDE-17)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,3,3',4,4',5,6-HeptaBDE (BDE-190)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,3',4,4'-TetraBDE (BDE-66)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,3',4',6-TetraBDE (BDE-71)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
2,4,4'-TriBDE (BDE-28)		1.3 – 14.4	pg/L	1614 Draft	Axys Analytical
DecaBDE (BDE-209)		569	pg/L	1614 Draft	Axys Analytical
acetaminophen	60		ng/L	LC/MS/MS	Axys Analytical
carbamazepine	1.5		ng/L	LC/MS/MS	Axys Analytical
codeine	3		ng/L	LC/MS/MS	Axys Analytical
dehydronifedipine	0.6		ng/L	LC/MS/MS	Axys Analytical
diazinon	0.1		ng/L	LC/MS/MS	Axys Analytical
diltiazem	0.3		ng/L	LC/MS/MS	Axys Analytical
ethynylestradiol		50	ng/L	GC/MS	Axys Analytical
nonylphenol		10	ng/L	GC/MS	Axys Analytical
Perfluorobutanesulfonate		1.64	ng/L	LC-MS/MS	Axys Analytical
Perfluorodecanoate		0.48	ng/L	LC-MS/MS	Axys Analytical
Perfluorododecanoate		0.29	ng/L	LC-MS/MS	Axys Analytical

Parameter	LOQ	MDL	units	Method	Reference
Perfluoroheptanoate		0.59	ng/L	LC-MS/MS	Axys Analytical
Perfluorohexanesulfonate		1.14	ng/L	LC-MS/MS	Axys Analytical
Perfluorohexanoate		0.37	ng/L	LC-MS/MS	Axys Analytical
Perfluorononanoate		0.66	ng/L	LC-MS/MS	Axys Analytical
Perfluorooctanesulfonate		1.18	ng/L	LC-MS/MS	Axys Analytical
Perfluorooctanoate		0.5	ng/L	LC-MS/MS	Axys Analytical
Perfluoropentanoate		0.48	ng/L	LC-MS/MS	Axys Analytical
Perfluoroundecanoate		0.28	ng/L	LC-MS/MS	Axys Analytical
sulfamethoxazole	0.6		ng/L	LC-MS/MS	Axys Analytical
Triclosan	60		ng/L	LC-MS/MS	Axys Analytical
trimethoprim	1.5		ng/L	LC-MS/MS	Axys Analytical

[1]Method Detection Limit; [2]Limit of Quantitation LOQ represents the lowest standard in the calibration curve or, in instances where a standard curve is not specified by the procedure, LOQ represents the limitations of the method.

3.2 Sample Design

Table 5 lists potential sample sites. Due to limited funding, a subset of the potential sample sites will be sampled. In 2007, the sample sites will be sites E1, E4, E7, E9, E12 and E16. Sample sites are in the center channel because the estuary is well mixed at most locations. The fixed sample sites selected throughout Zones 2 through 5 replicate many of the sites sampled in previous chronic toxicity work sponsored by the DRBC and the sites are at or near locations routinely sampled for water quality as part of DRBC monitoring programs.

Main stem channel sites will be sampled. All samples will be collected at a depth of 0.6 of the water column using a 10 liter Niskin sampling bottle. Mainstem samples collected following DRBC methodology will be collected using General Oceanic's Niskin sampling bottle, Model 1010-1.2 configured to collect a vertical sample. At each location, grab samples shall be collected at three sites on a transect across the channel (center of the navigation channel, at the right edge of the channel, and at the left edge of the channel), and a transect composite made per location. The transect composites for each site sampled on each sample day will be transported to the contract laboratory for analysis.

The assessment to be made at each sampling location will include determination that the proper location (latitude and longitude) has been reached, that the proper sample depth is attainable, the salinity of the site is measured and that no dangerous conditions exist prior to and during sample collection.

For the physical-chemical analysis of ambient water, one field blank will be collected on each sample day. One (1) bottle blanks will be collected for parameter analysis.

Table 5: Potential Sampling Locations

Site	RIVER MILE	ZONE	SITE DESCRIPTION	LANDMARKS	LATITUDE (dd.ddddd)	LONGITUDE (dd.ddddd)
E1	*50*	*5*	*Liston Point*	*Buoy 8L*	*39.45500*	*75.5600*
E2	55	5	Reedy Island	Buoy 6R	39.51278	75.55333
E3	63.0	5	N. of Pea Patch Island	Buoy 2B; Electric Towers	39.61431	75.57708
E4	*68.1*	*5*	*S. of De. Memorial Bridge*	*Between Buoys 1C & 2C*	*39.65472*	*75.54667*
E5	70.8	5	N. of De. Memorial Bridge	Buoy CR	39.71908	75.50425
E6	75.1	5	Opposite Oldman's Point	Buoy 6B	39.76869	75.47303
E7	*80.0*	*4*	*Opposite Mouth of Marcus Hook Creek*	*S. of Buoy 9M*	*39.81336*	*75.39058*
E8	85	4	Eddystone	N. of Buoy 1E	39.850550	75.327090
E9	*90*	*4*	*South of Schuylkill River*	*NA*	*39.88350*	*75.18616*
E10	95.5	3	Opposite Mouth of Big Timber Creek	N. of Buoy 48	39.88522	75.14075
E11	99.4	3	Penn's Landing	Penn's Landing	39.94547	75.13600
E12	*105.4*	*3*	*Mouth of Pennsauken Creek*	*N. of Buoy 5*	*39.99478*	*75.05978*
E13	111.5	2	Mouth of Rancocas Creek	Buoy 22	40.04831	74.97589
E14	115.0	2	Beverly	Buoy 30	40.07053	74.92750
E15	122	2	Florence	Buoy GC 63	40.123980	74.803510
E16	*131.1*	*2*	*Biles Channel*	*Buoy GC 101*	*40.181560*	*74.745050*

2007 sample sites are in italics.

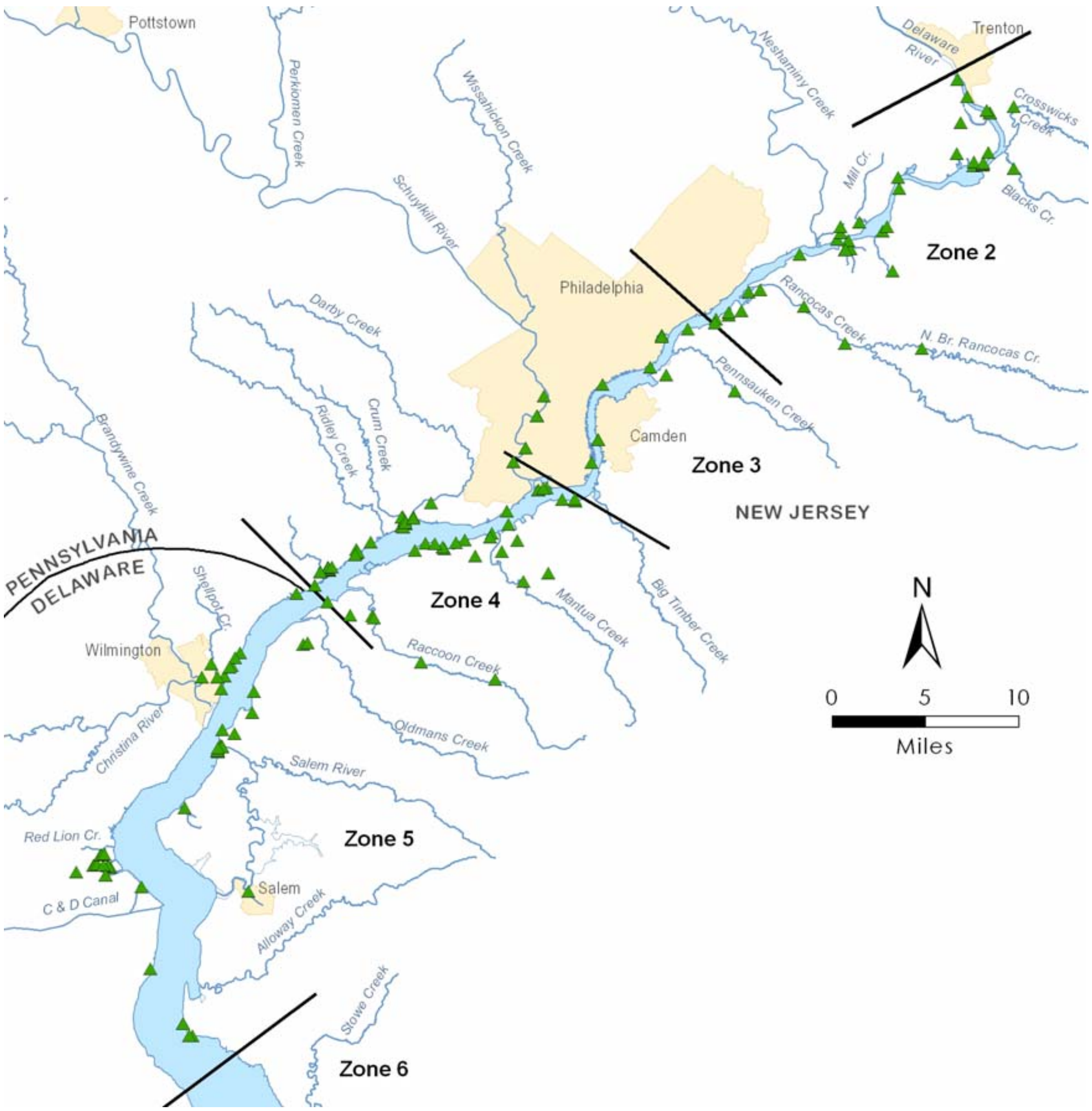


Figure 2. Tidal Delaware River Dischargers

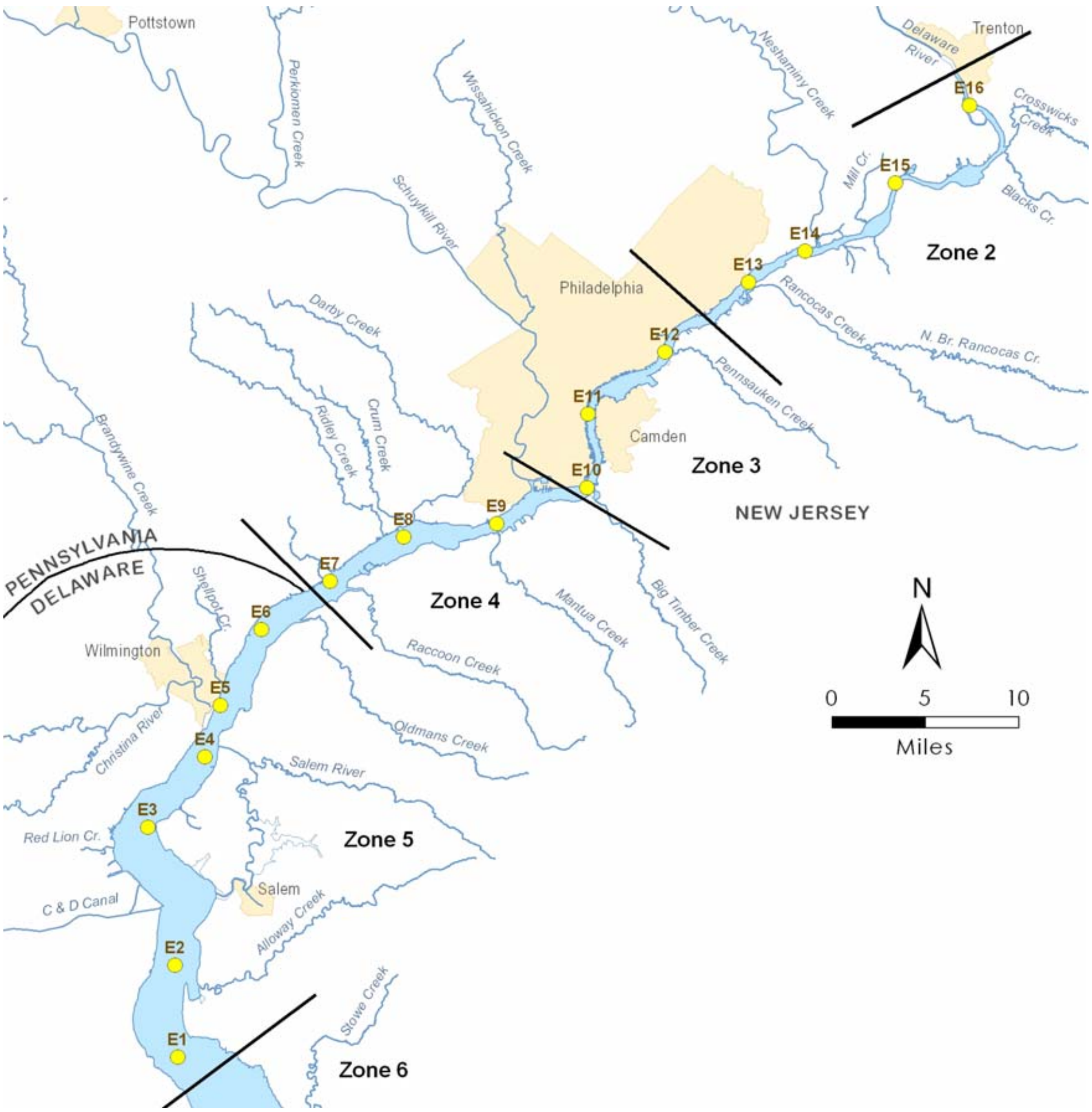


Figure 3: Potential Sampling Sites

3.2.1 Decontamination of Field Sampling Equipment

Each item of field sampling equipment, which will come into direct contact with a sample, will be decontaminated by the following decontamination procedure prior to each sampling survey:

1. Soak for a minimum of 15 min with a non-phosphate detergent solution prepared with tap water, in accordance with the manufacturer's instructions. Scrub equipment using a clean bristled brush. Change the position of the equipment during the soak time to assure contact with the soap (e.g., roll canisters periodically).
2. Triple rinse with Milli-Q water.
3. Careful rinse once with fresh, dilute (10%, V:V) hydrochloric or nitric acid
4. Triple rinse with Milli-Q water.
5. Single acetone rinse. (For Niskin bottles and plastic funnels substitute a methanol rinse for the acetone rinse)
6. Triple rinse with Milli-Q water.
7. Air dry.
8. Re-assemble equipment and wrap with plastic bags or cover with aluminum foil.

Field equipment will be closed and wrapped in plastic during storage and transport to sampling sites.

Between sampling locations, all field equipment coming into contact with water sampling will be rinsed with Milli-Q water, rinsed with methanol, and double-rinsed with Milli-Q water.

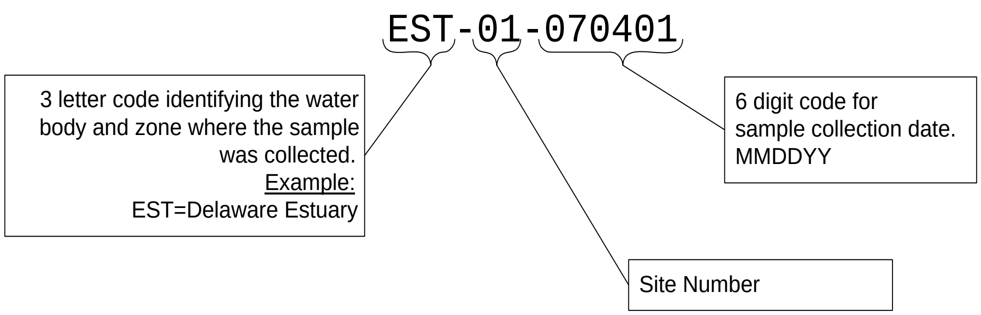
Milli-Q water may be replaced with equivalent high quality water.

Cubitainers are pre-cleaned and do not require decontamination

3.2.2 Sample ID and Labeling

A unique sample ID shall be assigned to each sample. The sample ID shall incorporate the body of water where the sample was collected, site identification, and sample collection data as shown below. All the bottles will be labeled with sample numbers and locations. Sample labels are to be completed for each sample using waterproof ink.

Figure 4. Sample Identification Key



3.2.3 Sample Preservation, Holding, and Transportation

To minimize microbial degradation and chemical transformation, the sample collection team shall preserve samples by chilling the samples on ice at the site, during transport, and until receipt by the lab. The samples will be transported and stored at 4 ^{o}C ± 2 ^{o}C . The temperature inside coolers will be tracked during transport with a temperature log.

Upon arrival at the laboratory, samples are logged in and temperature is measured and recorded. If the samples are not immediately prepared for testing, they are stored at 4 ^{o}C ± 2 ^{o}C until used. The holding time from sample collection to first use must not exceed 36h.

4. DATA REVIEW

Data elements generated by this project will undergo a review process prior to their release in report form. There will be various levels of review scheduled to ensure that the data generated are valid (Table 6).

Non-compliant QC will be documented in accordance with the ELS QA Assurance Management Plan. For example, non-compliant QC will be reported in an excerption report and data that are not within acceptable criteria will be reported with a qualifier code.

Table 6: Data Review

Process	Person(s)	Review Step
Verification Toxicity and Analytical	Project Officer QA/QC Officer	Review if data required for the project are available (Completeness check)
Validation Toxicity and Analytical	Project Officer QA/QC Officer	Check compliance with method or procedure requirements and performance criteria
Usability Assessment Toxicity and Analytical	Project Officer QA/QC Officer	Assess usability of data to meet project quality objectives
Analytical Data reduction, review and reporting	Axys Analytical Services and CBL QA/QC Officers	Analytical data reduction, review and reporting including non-compliance will follow the QA Assurance Management Plan for the contract labs.

5. PROJECT SCHEDULE

Activity	5/07	6/07	7/07	8/07	9/07	10/07	11/07	12/07	1/08	2/08	3/08	4/08	5/08
QAPP Development	X	X											
QAPP EPA Approval		X	X	X	X								
Sampling						X	X						
Toxicity Testing						X	X						
Phys-Chem Analysis of Ambient Water							X	X	X				
Data Review								X	X	X			
Data Analysis									X	X	X		
Data Evaluation										X	X		
Report Generation											X	X	X

6. REFERENCES

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