Delaware Ambient Statewide Surface Water Quality Monitoring Program

Quality Assurance Project Plan

Prepared By
Robin M. Tyler Ph.D.

In Collaboration With
The Watershed Assessment Section
The Environmental Laboratory Section

March 2007

Delaware Department of Natural Resources and Environmental Control
Division of Water Resources
Watershed Assessment Section
Environmental Laboratory Section

Revised March, 2007 by Robin M. Tyler, Ph.D.
Environmental Scientist IV, Environmental Laboratory Section
In; Water Shared Files F:\R Tyler

Table of Contents

List of Tables

List of Figures

Approval Signatures

Quality Assurance Project Plan

Delaware Statewide Ambient Surface Water Quality Monitoring Program

USEPA Region 3

Project Officer Signature _____
Project Officer Larry Merrill, Office of Watersheds

Project QA Officer Signature _____
Project QA Officer Patricia Iraci, Office of Watersheds

State of Delaware

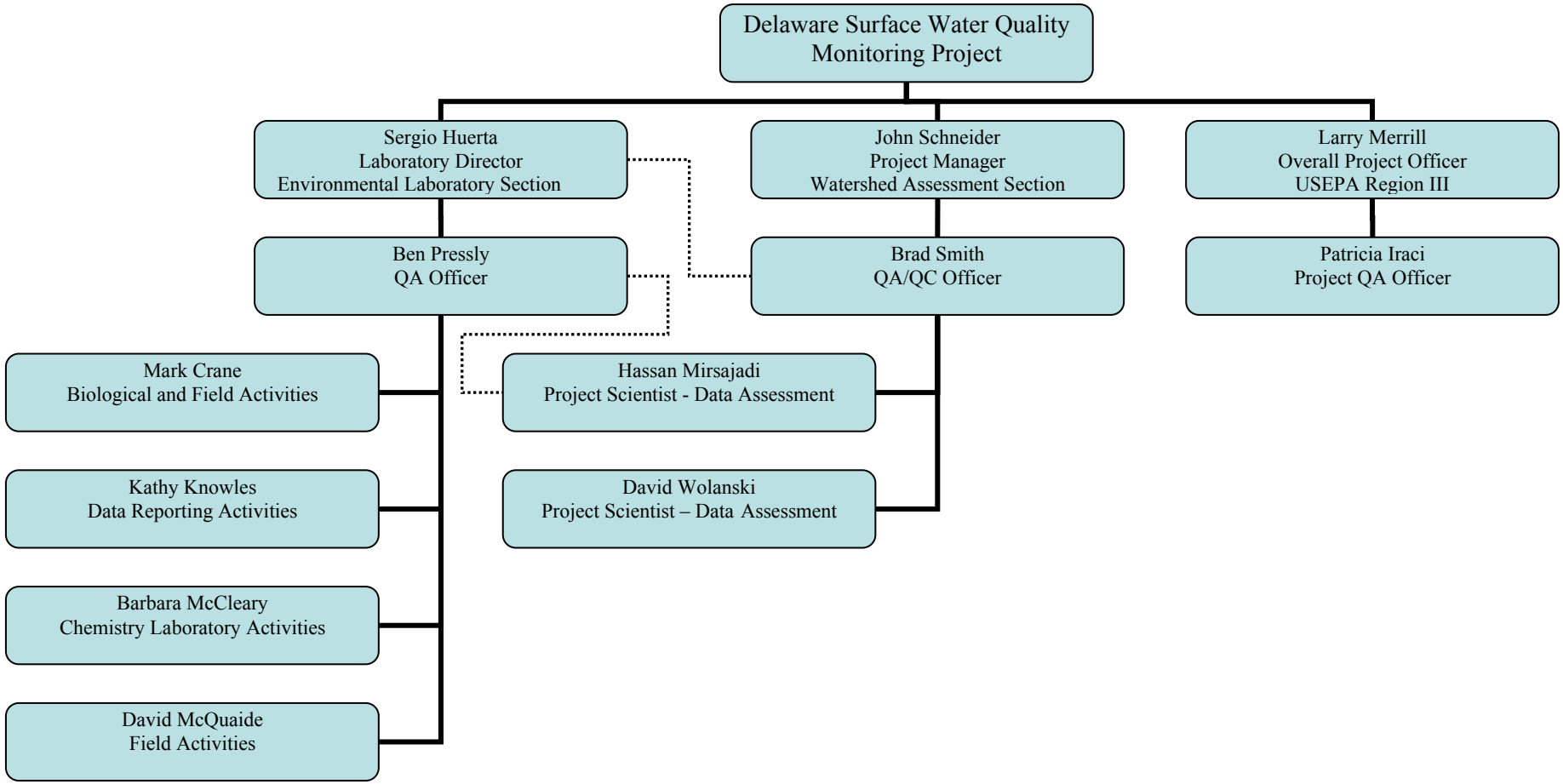
Project Manager Signature _____
Project Manager John Schneider, Watershed Assessment Section

Project QA/QC Officer Signature _____
Project QA/QC Officer Brad Smith, Watershed Assessment Section

Laboratory Director Signature _____
Laboratory Director Sergio Huerta, Environmental Laboratory Section

Laboratory QA Officer Signature _____
Laboratory QA Officer Ben Pressly, Environmental Laboratory Section

Project Management



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Background

The Delaware Department of Natural Resources (DNREC), Division of Water Resources (DWR), Watershed Assessment Section (WAS) is responsible for the monitoring of physical, chemical and biological parameters in ambient surface waters throughout the State and does so via the Ambient Surface Water Quality Monitoring Program (ASWQMP). The resulting data and information are used to pursue the following objectives:

1) Define current water quality conditions.
2) Identify and define long-term trends in water quality.
3) Determine the suitability of Delaware waters for designated uses (e.g. water supply; recreation; fish, aquatic life and wildlife) as specified in the Delaware Surface Water Quality Standards.
4) Determine whether the water quality standards are being met.
5) Identify and prioritize high quality and degraded waters.
6) Support the Total Maximum Daily Load Program.
7) Evaluate the overall success of Delaware's water quality management efforts.

The findings are reported biannually to the United States Environmental Protection Agency (EPA) in the Water Quality Inventory Report as mandated by Section 305(b) of the Clean Water Act (CWA), and are used to identify and prioritize water-quality limited waters as mandated by Section 303(d) of the CWA, as well as waters of high quality. Since the late 1990's the data have been used to develop and calibrate TMDL models, and in the future will be used to gage the success of TMDL-based Pollution Control Strategies. The ASWQMP monitoring design is targeted (judgmental) in contrast to random (probabilistic) due in large part to addressing objectives 2 and 6 above.

The collection of ASWQMP samples and field data is conducted by the DNREC, DWR, Environmental Laboratory Section (ELS). The analysis of samples and generation of analytical results is also done by the ELS, with exception of some tests which are outsourced to selected laboratories that have EPA-approved Quality Assurance Management Plans. This Quality Assurance Project Plan (QAPP) covers monitoring activities planned for Calendar Year 2006 and defines and/or references the quality control procedures and methodologies applicable to three of the five components of the ASWQMP. These three components are:

(1) General Assessment
(2) Total Maximum Daily Loads/Special Projects
(3) Biological Assessment

Throughout Calendar Year 2006 grab sample monitoring will be conducted for a routine complement of physical and chemical parameters at 183 stations distributed Statewide. The sampling frequency will be either bi-monthly or monthly. Some of these stations will be monitored for a selected group of metals. Also throughout 2006, an onsite, portable automated laboratory will be deployed at a key TMDL site to intensively monitor selected eutrophication

indicator parameters under various environmental conditions, the results from which will illuminate the response of the Inland Bays to the Pollution Control Strategy. From April through October and at hourly intervals, automated multi-parameter sondes will be deployed at several (5-10) stations in the Piedmont major drainage basin to monitor dissolved oxygen and other parameters known to fluctuate widely over short (minutes to hours) time scales (i.e. temperature, pH, and specific conductivity). During autumn, biology and habitat conditions will be sampled once at 50 stations, each of which are on the 303(d) list due to previous diagnosis of impaired biology or habitat.

It is very important to note that the collection of the data necessary to develop TMDL models was completed at the end of Calendar Year 2005 (1st half of Fiscal Year 2006) and that future monitoring tasks such as those summarized in the previous paragraphs will be oriented toward tracking the progress of the subsequent respective Pollution Control Strategies.

Project/Task Description

The monitoring design for the ASWQMP is targeted (judgmental) in contrast to random (probabilistic) due in large part to meeting the program objectives of (1) defining long-term trends and (2) documenting and quantifying the effectiveness of TMDL-based Pollution Control Strategies (i.e. best management practices, retrofit/restoration actions).

General Assessment

Section 305(b) of the CWA requires States to monitor their ambient surface waters in order to ascertain the extent to which quality is adequate to provide for the protection and propagation of a balanced population of shellfish, fish, and wildlife and allow recreational activities in and on the water. Over the last three decades Delaware has met this requirement via the General Assessment. Since the mid-1990's data from the General Assessment has also contributed to the development of TMDL models that specify the levels to which pollution loads must be limited in order to for the protection and propagation of aquatic life and allow recreation. The monitoring activities described in this QAPP plan begin in calendar year 2006 and represent an increase in monitoring frequency at General Assessment Monitoring Network (GAMN) stations from 4-6/year to 6-12/year. The increase in GAMN monitoring frequency is needed to offset the conclusion of TMDL-specific monitoring so that the responses of aquatic systems to the implementation of TMDL-based Pollution Control Strategies can be properly assessed.

The GAMN divides Delaware into four major drainage basins that are collectively divided into 45 sub-basins (Figures 1 and 2a-d)). Statewide, the GAMN includes 182 stations and monitoring occurs at multiple stations within each major basin (Table 1, Attachment 1). The records for many of these stations are long-term (years to decades) and are being used to define trends in water quality. All GAMN stations are monitored for temperature, salinity, dissolved oxygen, pH, alkalinity, hardness, chloride, chlorophyll, biological oxygen demand, total suspended solids, turbidity, organic carbon, nutrients, and Enterococcus bacteria (Table 2). Tidal

waters and lakes/ponds are also monitored where and when possible for water clarity (Secchi depth) and light attenuation (Table 2). Some nontidal and tidal stations are further monitored for metals (Table 3) while some nontidal stations are monitored for biology/habitat.

The GAMN data are entered into the STORET database and analyzed to (1) define the water quality status and trends for each sub-basin and (2) compare the data with water quality standards to assess designated use support as mandated by Section 305(b) of the CWA. The findings are published every 2 years in the Water Quality Inventory 305(b) Report.

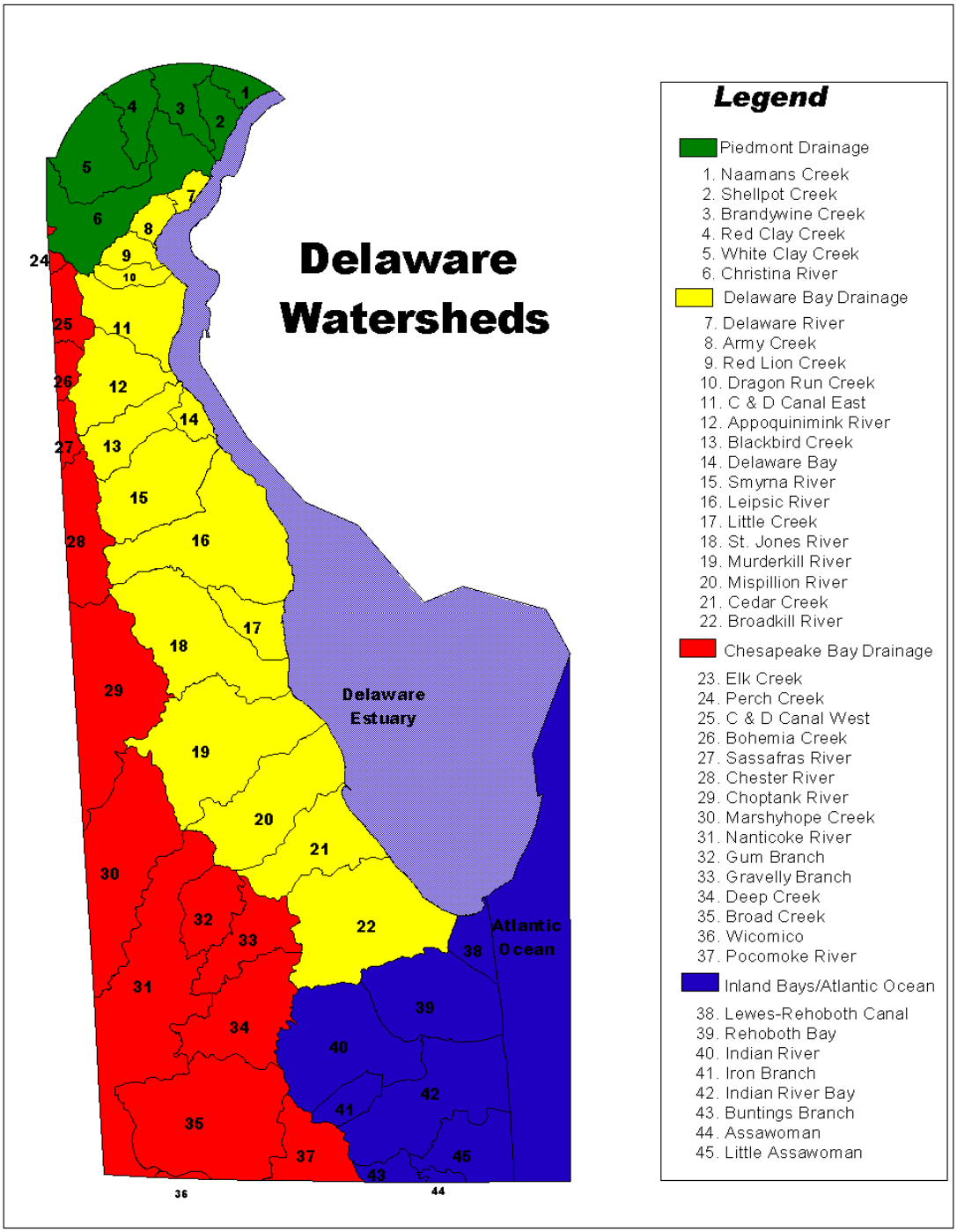

Figure 1: State of Delaware partitioned into four major drainage basins (color-coded) and sub-basins (numbered).

Figure 2a – This map provided electronically in PowerPoint file *Figure 2a-d*.

Figure $2b_1$ - This map provided electronically in PowerPoint file *Figure 2a-d*.

Figure $2b_2$ - This map provided electronically in PowerPoint file *Figure 2a-d*.

Figure $2c_1$ - This map provided electronically in PowerPoint file *Figure 2a-d*.

Figure $2c_2$ - This map provided electronically in PowerPoint file *Figure 2a-d*.

Figure 2d - This map provided electronically in PowerPoint file *Figure 2a-d*.

Table 1 – This table provided electronically in Excel file *Table 1 and Attachment 1*.

Table 2: Chemical and physical water quality parameters to be analyzed at all Stations in the General Assessment Monitoring Network during Calendar Year 2006. For acute and chronic criteria for the protection of aquatic life in freshwater and marine systems see Table 1 of the State of Delaware Surface Water Quality Standards (State of Delaware 2004).

Parameter	*Method Reference (EPA)*	*Reporting Level*	*Container*	*Preservation*	*Holding Time*
Water Column Nutrients					
Total Phosphorus	EPA365.1 M	0.005 mg/l P	HPDE 2L	Cool to ≤6°C, dark, digest within 7 days	28 days
Soluble Ortho-phosphorus	EPA365.1	0.005 mg/l P	HPDE 2L	Filter, Cool to ≤6°C, dark	48 hours
Ammonia Nitrogen	EPA350.1	0.005 mg/l N	HPDE 2L	Cool to ≤6°C, dark, H_2SO_4 to pH < 2	28 days
Nitrite+Nitrate N	EPA353.2	0.005 mg/l N	HPDE 2L	Cool to ≤6°C, dark, H_2SO_4 to pH < 2	28 days
Total N	SM 4500 NC	0.08 mg/l N	HPDE 2L	Cool to ≤6°C, dark, digest within 7 days	28 days
Carbon and Organics					
Total Organic Carbon	EPA415.1	1 mg/l	HPDE 2L	Cool to ≤6°C, dark, HCl to pH < 2	28 days
Dissolved Organic Carbon	EPA415.1	1 mg/l	HPDE 2L	Filter, Cool to ≤6°C, dark, HCl to pH < 2	28 days
Chlorophyll-a (Corr)	EPA 445.0	1 µg/l	HPDE 250 ml	Filter, Freeze filter	30 days
Biochemical Oxygen Demand					
BOD_5, N-Inhib (CBOD)	SM20thed-5210B	2.4 mg/l	HPDE 2L	Cool to ≤6°C, dark	48 hours
BOD_{20}, N-Inhib (CBOD)	SM20thed-5210B	2.4 mg/l	HPDE 2L	Cool to ≤6°C, dark	48 hours
General					
Total Suspended Solids	EPA160.2	2 mg/l	HPDE 2L	Cool to ≤6°C, dark	7 days
Alkalinity	EPA310.1	1 mg/l	HPDE 2L	Cool to ≤6°C, dark	14 days
Hardness	EPA130.2	5 mg/l	HPDE 2L	Cool to ≤6°C, dark, H_2SO_4 to pH < 2	6 months
Chloride	EPA325.2	1 mg/l	HPDE 2L	Cool to ≤6°C, dark	28 days

Turbidity	EPA180.1	1 NTU	HPDE 250 ml	Cool to ≤6°C, dark	48 hours
Dissolved oxygen – Winkler[2]	EPA360.2	0.25 mg/l	Plastic 300 ml BOD	Onsite Fixation with Manganous sulfate and Alkali-iodide-azide, store in dark	8 hours
Dissolved oxygen – Field	EPA360.1	0.1 mg/l	NA	NA	NA
pH – Field	EPA150.1	0.2 pH units	NA	NA	NA
Specific Conductivity – Field	EPA120.1	1 µS/cm	NA	NA	NA
Salinity – Field	SM20thed-2520B	1 ppt	NA	NA	NA
Temperature – Field	EPA170.1	0.1 ^{o}C	NA	NA	NA
Secchi Depth[3]	EPA/620/R-01/003	0.1 Meters	NA	NA	NA
Light Attenuation[4]	EPA/620/R-01/003	%	NA	NA	NA
Bacteria					
Enterococcus	SM20thed-9230C	1 cfu/100 ml	Factory-sealed, presterilized 125 ml sterile plastic (HDPE or PP) container	Sodium thiosulfate pre-added to containers in the laboratory. Cool to ≤6°C; dark.	STAT: 6 hrs

Footnotes:

[1] The Reporting Level refers to the lowest level detectable by a method. Limit of Quantitation (LOQ) is defined as 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. For those tests where reference spiking material exists, the Method Detection Limit (MDL), is defined in the Federal Register 40 CFR Part 136 Appendix B. MDL values are generated or verified once per year. Results less than the MDL are considered to be not detected and "< MDL" is reported. Results greater than the MDL, but less than the LOQ, are qualified with a J to indicate a result that is extrapolated or estimated. For tests where MDL is not applicable, results less than the LOQ are reported as "< LOQ". The Laboratory's MDLs must meet or exceed (i.e., are lower than) the reporting level requirements listed in Table 2.

[2] Dissolved oxygen to be performed by the Winkler method when the salinity is > 5ppm

[3] Secchi Depth to be measured at designated stations.

[4] Light attenuation to be conducted as practical to obtain correlation with Secchi disk readings.

Table 3: Metals parameters to be analyzed at some stations in the General Assessment Monitoring Network during Calendar Year 2006 (See Attachment 1). For acute and chronic criteria for the protection of aquatic life in freshwater and marine systems see Table 1 of the State of Delaware Surface Water Quality Standards (State of Delaware 2004).

Metals (dissolved and total)	***Method Reference (EPA)***	***Reporting Level***	***Container***	***Preservation***	***Holding Time***
Copper	EPA 200.7 M	5.0 ug/l	HPDE 500 ml. See footnote.	Cool to ≤6°C, dark. HNO_3 to pH <2. See footnote.	6 months
Lead	EPA 200.7 M	3.0 ug/l	HPDE 500 ml See footnote.	Cool to ≤6°C, dark. HNO_3 to pH <2. See footnote.	6 months
Zinc	EPA 200.7 M	10 ug/l	HPDE 500 ml See footnote.	Cool to ≤6°C, dark. HNO_3 to pH <2. See footnote.	6 months
Arsenic	EPA 200.7 M	10 ug/l	HPDE 500 ml See footnote.	Cool to ≤6°C, dark. HNO_3 to pH <2. See footnote.	6 months
Chromium (hex) - Dissolved	SM13thed-117A	10 ug/l	HPDE 500 ml See footnote.	Cool to ≤6°C, dark. See footnote.	24 hours
Iron	EPA 200.7 M	100 ug/l	HPDE 500 ml See footnote.	Cool to ≤6°C, dark. HNO_3 to pH <2.See footnote.	6 months

Footnote: Total metals samples are collected in pre-acidified HPDE bottles. Dissolved metals samples are also collected in HPDE bottles that are not pre-acidified. Filtration of samples for dissolved metals is done at the laboratory on the day of collection. Samples are acidified immediately after filtration.

Total Maximum Daily Load (TMDL)

Section 303(d) of the CWA requires States to identify and prioritize their waterbodies, or segments of waterbodies, that are water-quality-limited, and to develop TMDL models for problem pollutant/s. A water-quality-limited waterbody is defined as not meeting water quality standards, and/or not expected to meet standards, after application of technology-based effluent limitations for Publicly Owned Treatment Works and other point sources. The TMDL development schedule is coordinated with the Department's Whole Basin Management Program and is included in a court-approved Consent Decree (American Littoral Society, et al. vs. United States EPA et al., Civil Action No. 96-5920).

Delaware has developed a 303(d) list of water-quality-limited waters, has been in the process of developing TMDL models for listed segments since the late-1990's, and is on track to complete this process in the near future. Monitoring for the specific purpose of TMDL model development was completed at the end of Calendar Year 2005 (mid-point Fiscal Year 2006). Depending upon basin size and the amount and type of human activity the number of stations required to develop a TMDL model can be substantial. Stations at which data is gathered for the sole purpose of TMDL model development are active only for as long as necessary to develop the model and are therefore short-term (one to a few years). The parameters monitored at TMDL stations are the same as at the GAMN stations and it is important to keep in mind that GAMN stations are included in the full complement of stations used to develop the TMDL model.

The output of a TMDL model is the basis for development of a Pollution Control Strategy (PCS), which sets the loading limits of targeted pollutants to a 303(d) waterway and establishes the means by which these limits are achieved. The amount of data required to confidently pronounce whether or not the PCS limits are being met exceeds that which has been historically collected at the GAMN stations (sampling frequency 4-6 events per year), thus the need to expand the GAMN sampling frequency to 6-12 events per year as noted above in the GAMN description subsection. The degree of success of a respective PCS will eventually be reflected in the long-term trend of the GAMN stations within the respective basin. Therefore, beginning with Calendar Year 2006 the net amount of monitoring effort heretofore channeled into many stations within a few sub-basins each year for TMDL development has been redistributed to a smaller number of stations (GAMN) over the entire complement of sub-basins which have a PCS.

Special Projects

A special project is warranted when a water quality issue cannot be adequately addressed within the scope of GAMN or TMDL monitoring. The results from special projects are also included in the Water Quality Inventory 305(b) report. Special projects that are planned for initial implementation, or continuation, in 2006 are:

Continuous Monitoring

On-Site Portable Laboratory

A portable, automated on-site laboratory was deployed in 2005 at the outlet to Millsboro Pond which is located at the head of tide in Indian River, the largest tributary of the Inland Bays. This monitoring will continue in 2006. The purpose of the project is to track the effectiveness of the TMDL-based Pollution Control Strategy in that sub-basin. The laboratory collects and analyzes samples at programmed intervals for inorganic nitrogen and phosphorus (nutrients) and other parameters (Attachment 2). Flow volume is also measured continuously at this station by the United States Geological Survey (USGS), making it possible to define inorganic nitrogen and phosphorus loads entering the Inland Bays via the nontidal segment of Indian River.

Multi-Parameter Sondes

For the past several years, the WAS has been developing a network of water quality monitoring stations at which data is collected continuously for dissolved oxygen concentration and % saturation and other parameters (temperature, specific conductivity, pH, and salinity) that exhibit substantial fluctuation over short time scales such as the diel (24-hour) cycle or in response to weather conditions. This monitoring is conducted using Yellow Springs Instruments (YSI) 6-series multi-parameter sondes. "Continuously" with respect to sonde monitoring means that measurements will be taken at least every 15 minutes when the instruments are deployed.

A rotating basin approach is planned, beginning with the Piedmont major basin and proceeding through the Chesapeake, Inland Bays and Delaware Bay basins in subsequent years (Figure 1). Sonde station locations have yet to be finalized and will be formally documented as an attachment to this QAPP at such time.

Also, the WAS, in cooperation with the USGS, will operate a number of additional continuous monitoring sites designed to work exactly like those stations previously mentioned with the exception that these sites will be equipped with telemetric hardware. This will allow remote contact with the instruments at any time in addition to transmitting, posting, and accessing the data over the web at near real-time.

Shellpot Creek Iron Study

Past monitoring of Shellpot Creek (Piedmont Basin) has shown excursions above the freshwater chronic criterion for iron of 1mg l^{-1} (there is no acute criterion) (State of Delaware 2004). The purpose of the study is to determine if the elevated iron concentrations are a naturally-occurring local phenomenon or a product of industrial activity in the vicinity.

This new special project adds one station along a small stream directly adjacent to the Shellpot drainage basin which, along with the two existing GAMN stations in the Shellpot basin, will be monitored monthly during Calendar Year 2006. The iron data from the special station will be compared with that from the GAMN Shellpot stations, and stations located on the Delaware River that are sampled under another project.

Biological and Habitat Monitoring

A long-term project is in progress to collect biological and habitat data from nontidal wadable streams in order to relate water quality conditions with biological integrity. Eligible stations must (1) be completely nontidal, (2) have perennial flow, and (3) be uninfluenced by elevated temperature resulting from lentic discharge (i.e. millpond, stormwater pond, etc). The biological data consists of two instream matrices: macroinvertebrate, and periphyton (first initiated in spring - 2005). The habitat data consists of instream and riparian zone matrices.

303(d) Sampling

Beginning in 2006 and every other autumn thereafter, biological (macroinvertebrate), habitat and chemical sampling will occur under baseflow conditions at 50 stations located along streams that have been placed on the 303(d) list due to impaired biology or habitat. This bi-annual sampling will rotate by county, major basin, or both. In the fall of 2006, the Piedmont major basin is targeted. Conjunctional chemical sampling will include all the parameters listed in Table 2 with exception of Enterococcus bacteria, which will not be sampled.

The data will be evaluated to determine whether any form of impairment still exists at each respective station. If impairment is concluded, then effort will be made to identify the cause/s. The procedure for identifying causation is not yet fully outlined but will likely follow the EPA Stressor Identification Guidance Document (USEPA, 2000).

General Evaluation of Biological Condition in Streams

In years between 303(d) sampling up to 50 GAMN stations will be sampled. The biological and habitat methodology will be the same as used for the 303(d) sampling. This general evaluation effort will include the periphyton sampling introduced previously. The immediate objective of this sampling is to determine the overall biological condition of nontidal streams in Delaware. The extended objective is to identify trends in biological condition in these waters.

Sampling, Analysis, Data Management, and Reporting

Water Sample Collection

All water sample collections will be conducted by the Field Services Branch according to ELS Operational Procedure, Surface Water Sampling, Revision 01-0600. *In:* ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3). Table 1 and Attachment 1 identify the sub-basins and stations to be monitored during 2006, respectively, while Tables 2 and 3 list the parameters to be measured. Method references and reporting levels for each parameter are also provided in Tables 2 and 3. Standard operating procedures for each parameter are provided electronically as Word Documents in the folder *SOPs applicable to 2006 ASWQMP*.

Instruments used to take measurements in the field (i.e. SonTech flow meter, YSI Data logger/sonde - dissolved oxygen, temperature, pH, specific conductivity) will be examined at the beginning of each field day to ensure good working order. At each nontidal stream that can be waded flow volume will be measured according to ELS Work Instruction Procedure (Flowtracker, Revision 01-0804), so that nutrient loading estimates can be subsequently calculated. All other field measurements, with exception of water clarity, will be taken using the YSI Datalogger/sonde unit according to ELS Work Instruction Procedure (YSI Multiparameter Display System, Revision 01-0705). Continuous monitoring usage of sondes will be conducted

according to ELS Operational Procedure YSI data sonde, Revision 01-1199. In tidal waters, effort will be made to collect samples at (or near) low slack tide, starting at the most downstream station and moving upstream. The station distribution in some watersheds requires that some stations be accessed by automobile and others by boat – thus two days are needed to sample all stations. Whenever possible the two days will be scheduled consecutively.

For routine physical and chemical parameters, the number of samples per site is shown in Table 1, which calls for the collection of 879 samples at the 182 GAMN stations and the 1 Shellpot Special Project stations through Fiscal Year 2006 (through June). Over the remaining months of Calendar Year 2006, the same sampling strategy will be continued, thus doubling the number of samples through December of 2006, assuming stable funding in Fiscal Year 2007.

One blank will be included with each sampling event. At least one station will be sampled in duplicate during each sampling event irregardless of the number of samples. Such "field" duplicates will be collected in the same manner as the given site's primary sample. Whenever the sampling event exceeds 10 stations an additional field duplicate will be collected for each group of 10, or fewer, additional samples that are collected. Thus a sampling event that has 15 samples will have two field duplicates while a sampling event of 25 samples will have three field duplicates.

Biological Sample Collection

Biological (macroinvertebrate, habitat, and periphyton) monitoring will be conducted by the Ecological Assessment Branch. Each field team will be led by a scientist who has at least 10 years of experience in nontidal stream sampling of freshwater macroinvertebrates.

Biology and habitat sampling that occurs in the Middle Atlantic Coastal Plain Ecoregion, which accounts for 90 % of Delaware and includes all of three major basins (Delaware Bay, Chesapeake Bay, Inland Bays) will be done in accordance with methods defined in USEPA (1997). Biology samples will be collected at coastal plain sites using a D-framed net.

Biology and habitat sampling that occurs in the Northern Piedmont Ecoregion, a relatively small area located in the northern most part of Delaware and representing the remaining 10 % of the State will be conducted according to methods defined in Rapid Bioassessment Protocols for use in Wadable Streams and Rivers (EPA 841-B-99-002). Biology samples will be collected at piedmont sites using a kick net.

Periphyton sampling will be conducted according to the USGS, National Water Quality Assessment Program (Moulton et al. 2002). Samples will be collected from natural substrates, sticks and/or macrophytes (coastal plain), and rocks (piedmont). Only sticks that have obviously been in the water for an extended period (weeks to months) will be sampled.

Variability of the macroinvertebrate and periphyton communities within stations will be addressed by collecting triplicate samples at three of the 50 stations. D-net and kick-net contents will be transferred to a sieve bucket (600 µ mesh) where large pieces of detritus (e.g. leaves and

sticks) will be rinsed and removed. Samples will be preserved in the field. Macroinvertebrate samples will be preserved in 90 % ethanol solution (alcohol), periphyton samples in buffered formalin.

Sample Handling and Custody

Sample handling and custody forms are used to document information such as sample location, time and method of collection, preservation techniques, other relevant field metadata, laboratory receipt, laboratory custody, and disposal (see Attachment 3, ELS Quality Assurance Management Plan - Dec. 2002, Section 7). These links ensure sample integrity from collection, through analysis to disposal. Field personnel or the Project Manager will initiate the Field Chain of Custody Form. Samples will be transported to the laboratory within required holding times.

Laboratory Analysis of Water Samples

Laboratory instrument testing, inspection and maintenance procedures are described in the ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3, Sections 7 and 8).

Methods and frequency of calibration/service of laboratory equipment are described in detail in the ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3, Sections 7 and 8).

Laboratory QC procedures will be performed including: analytical spikes, calibration check standards, instrument blanks, internal standards, laboratory control samples (LCS), laboratory control sample duplicates (LCSD), and matrix spikes (MS). These procedures are defined in greater detail in the ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3, Section 7).

Some supply items are reusable (e.g. bottle ware). Sample bottles and fixatives are maintained by the laboratory. The ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3, Section 7) includes quality control procedures designed to prevent contamination of supplies.

Laboratory Analysis of Biological Samples

The field preserved macroinvertebrate samples will be outsourced for subsampling and identification to the lowest practical taxon. Potential contractors will be required to provide the following qualifications information;

- Description of work including all project tasks and how the project will be managed by the contractor.
- Detailed description of QA/QC procedures.
- Summary of experience with sorting and identification of nontidal macroinvertebrate samples in the region.
- Statement of Qualifications of all personnel involved in the work.

- Cost quotation.

One 200-organism subsample will be removed from each sample using a Caton subsampler. For samples with less than 200 organisms the entire sample will be picked and the paucity of organisms will be noted. Anticipated level of identification for each phylum is as follows;

- Arthropoda genus / some species
- Annelida genus / some species
- Mollusca genus / some species
- Bryozoa family / some genus (statoblasts)
- Platyhelminthes genus / some species
- Cnidaria genus

For analytical purposes, the species composition and abundance data will be reduced to the genus level. A multi-metric approach will be used to calculate a biological index (BI) for each sample which is expressed as a percentage of the ecoregion reference values (see Gibson 1996). Based on the BI, the site will then be categorized according to condition (i.e. excellent, good, moderately degraded, severely degraded).

The periphyton samples will be outsourced for identification to a contractor to-be-determined. The procedure used by the contractor who identified the 2005 samples, EcoAnalysts, Inc., (Periphyton Identification Procedure – see attached SOPs) explains how this type of analysis is generally done.

From each set of triplicate results (three stations sampled in triplicate for macroinvertebrates and periphyton) a coefficient of variation will be developed. The range of these three coefficients of variation will be regarded as the within-station spatial variability of the biological community across the entire study area.

Data Management

All completed field-generated and laboratory-generated data will be entered into the ELS Laboratory Information Management System (LIMS). Field calibration logs and laboratory calibration logs will be maintained at the ELS. Prior to converting the data into electronic format, field-generated data will be spot-checked for errors. Laboratory-generated data will be maintained in hardcopy and electronic format.

Review, Verification, and Validation

Field data, and laboratory analytical results, will be initially verified by the individual that collected or analyzed the sample, respectively. A second level review of the raw data is performed by an experienced peer, technical person, or supervisor in the laboratory. The second level review includes an assessment of the acceptability of the data with respect to correctness of numerical input, correctness of calculations and formulas, correct interpretation of outputs

(chromatograms, spectra, etc.), acceptability of QC data, and documentation that instruments were operating according to method specifications.

Verification and Validation Methods for Water Quality Samples

The data will be validated in accordance with the ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3). Field blank and field duplicate data provide additional validation of chemical data. Data entered manually from the field form, and electronically, will be visually checked to ensure that no data entry error occurred. ELS laboratory managers will be responsible for data verification and validation.

During data validation results of field samples and blanks (field and laboratory) greater than the MDL but less than the LOQ will be flagged with a "J" qualifier code, which will be regarded as an estimated value. Results associated with a contaminated laboratory blank or field blank will be flagged with a "B" qualifier code. These qualifiers will be included in the laboratory report and entered in STORET.

Data will be maintained within the ELS LIMS, Microsoft Access, and/or Excel, and will be delivered in a report to the Watershed Assessment Section. The data will also be entered into EPA's STORET database via the Water Quality Exchange (WQX).

Verification and Validation Methods for Biological samples

Subsampling efficiency will be evaluated (see SOP - Macroinvertebrate Subsampling Procedure). Enumeration of target organisms and selection of target organisms will be evaluated by the contractor. Selection of target organisms will also be evaluated by the DNREC. If the percent difference on any one sample is greater than 10 % then all sorted detritus will be returned to the contractor and resorted.

Ten percent of the identified subsamples will be cross checked by the DNREC for accuracy of data recording. Organisms will be identified, generally at the family or order level, and counted. Enumerations will be compared with the taxonomist's results. The relative percent difference (RPD) will then be calculated for each subsample and for each general taxonomic category. The acceptance criteria will be RPD $\leq$ 5.0 for all samples. Any sample with RPD > 5 will be returned to the contractor for re-identification and an additional 10 % will be checked. Taxa lists will not be modified based on the results of samples with $\leq$ 5.0 % difference because small differences can occur due to organisms lost in transfer to and from vessels, or stuck in eyedroppers and transferred to another sample.

In addition, 5 % of the total samples will be sent as blind samples to the USEPA office in Wheeling WV to be identified by the EPA biologists to the genus level (if possible). Upon completion, the contractor's lists for these samples will be provided to EPA and a QA report will be generated. Product from the contractor will include an ongoing reference collection of organisms. Up to 5 representatives of each taxon collected from past or present projects will be preserved in the collection. Reference organisms mounted on slides will be indicated as such.

Quality Assurance / Quality Control

Training Requirements/Certification

The ELS is fully certified by the EPA and other agencies to conduct field monitoring and sample analyses. The field staff, field biologists, and laboratory technicians and chemists are all properly trained to conduct the sample collection, sample analysis, and sample reporting tasks described in this QAPP.

Precision, accuracy, and detection limits for data collected/generated within the scope of this project are described in Section 7 of the ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3).

Issues of representativeness, completeness, and comparability are acknowledged and defined in Section 7 of the ELS Quality Assurance Management Plan - Dec. 2002 (Attachment 3).

Documentation and Records

The following documentation and records procedure will be followed for data collection:

a) The latest approved version of this Quality Assurance Project Plan will be distributed to project staff.
b) Field log books, field data sheets, field instruments, calibration logs, and raw data will be maintained by the DNREC-ELS Laboratory.
c) Records will be maintained for a period of 3 years following the completion of the project.
d) Analytical log books and laboratory instrument calibration information will be maintained at the DNREC-ELS Laboratory.
e) Macroinvertebrate and algal samples will be maintained at DNREC-ELS for a period of 3 years following completion of the project.

Transfer of Analytical Results to the Watershed Assessment Section

All analytical results including those from field duplicate samples, laboratory quality control samples (blanks, duplicates) and achievement of quality objectives (i.e., calibration, preservation, and spike recovery) shall be provided to the Watershed Assessment Section (WAS) digitally and on paper (using standard ELS data report forms). Any deviations from the above-referenced field or laboratory procedures or this sampling plan shall be documented in detail.

Data Assessment

Data assessment of the verified and validated water sampling results generated by, and transferred from the ELS will be conducted by the Watershed Assessment Section (WAS). The

assessment of the biological data and information will be conducted by the Ecological Assessment Branch and submitted in technical report form to the WAS. The topics of reporting as previously stated in the Background section of this QAPP are as follows:

1) Define current water quality conditions.
2) Identify and define long-term trends in water quality.
3) Determine the suitability of Delaware waters for designated uses (e.g. water supply; recreation; fish, aquatic life and wildlife) as specified in the Delaware Surface Water Quality Standards.
4) Determine whether the water quality standards are being met.
5) Identify and prioritize high quality and degraded waters.
6) Support the Total Maximum Daily Load Program.
7) Evaluate the overall success of Delaware's water quality management efforts.

Evaluation of the verified and validated results by the WAS will proceed according to the methodology for compiling the 305(b) Water Quality Inventory Report. The 305(b) Report is submitted biannually by the WAS to the EPA as mandated by the Clean Water Act (CWA), and the findings are used to identify and prioritize water-quality limited waters as mandated by Section 303(d) of the CWA, as well as waters of high quality. Since the late 1990's the data have been used to develop and calibrate TMDL models, and in the future will be used to gage the success of TMDL-based Pollution Control Strategies. The ASWQMP monitoring design is targeted (judgmental) in contrast to random (probabilistic) due in large part to addressing objectives 2 and 6 above.

Regarding field duplicates it is recognized that some waters exhibit substantial heterogeneity for some parameters over time scales of only a few minutes. Therefore for field duplicate samples, the two results will be averaged when they are reasonably similar (within 50 percent). For duplicates with disparity greater than 50 percent, the historical range of data for that parameter, at that station, will be examined and based on the best professional judgment of the project scientist the result most representative of the station will be used.

Limitations on the use of the data will be addressed in addition to reported findings. This will be done quantitatively using appropriate statistical tests when possible and by qualitative description otherwise.

Non-direct Measurements

Spatial data, including land use, soil, topography, and stream networks are frequently needed for conducting data analysis and preparing project reports. The source for all spatial Delaware-specific data will be the State of Delaware's digital warehouse at http://datamil.delaware.gov/ Precipitation data from NOAA weather stations and local monitoring stations (e.g. University of Delaware, New Castle County Airport) may be used to summarize storm information (intensity, duration). The DNREC regards all of these sources as reputable and their data will be taken at face value. Ancillary data from the scientific literature and DNREC's historic water quality database may also be used. The integrity of data from such sources will be considered case-by-case and usage will be contingent upon the professional judgment of the project scientists. All external data sources will be referenced.

References

State of Delaware. 2004. State of Delaware Surface Water Quality Standards: As amended July 11, 2004. Available from: Department of Natural Resources and Environmental Control, Division of Water Resources, Watershed Assessment Section, 820 Silver Lake Office, Plaza Suite 220, Dover, DE 19904

U.S. Environmental Protection Agency. 2000. *Stressor Identification Guidance Document.* 2000., Office of Water, Office of Research and Development, Washington DC. EPA/822/B-00/025

U.S. Environmental Protection Agency. 1999. Rapid Bioassessment Protocols for Use in Wadeable Streams and Rivers: Periphyton, Benthic Macroinvertebrates, and Fish. Office of Water, Office of Research and Development, Washington DC. EPA/841/B-99/002

U.S. Environmental Protection Agency. 1997. *Field and Laboratory Methods for Macroinvertebrate and Habitat Assessment of Low Gradient, Nontidal Streams*. Mid-Atlantic Coastal Streams (MACS) Workgroup, Environmental Services Division, Region 3, WV. 23 pp

Moulton S. R., J.G. Kennen, R. M. Goldstein, J. A. Hambrook. 2002. Revised Protocols for sampling algal, invertebrate, and fish communities as part of the National Water Quality Assessment Program. United States Geological Survey, Open-File Report 02-150. Reston Virginia Office

Attachments

1) Delaware Ambient Surface Water Quality Monitoring Program station locations, parameters monitored, and frequency of monitoring during Calendar Year 2006.

2) Portable on-site Laboratory - Aqualab product specification form.

3) State of Delaware 2002. Quality Assurance Management Plan for Laboratory and Field Operations, Environmental Laboratory Section, Division of Water Resources, Delaware Department of Natural Resources and Environmental Control, December 2002.