PENNSYLVANIA QUALITY ASSURANCE WORK PLAN

Chesapeake Bay Non-Tidal Network Water Quality Monitoring for Water Year 2018-21

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Preface

Pennsylvania's Non-tidal water quality monitoring Network (NTN) began in July 2005 with funding from EPA Section 117(d). The network, presently, is composed of 36 sites where nutrient and sediment concentrations are sampled on a fixed monthly basis and eight times per year during high flow events. These sites are monitored by the Susquehanna River Basin Commission (SRBC; 21 sites), and United States Geological Survey (USGS; 15) through project agreements with EPA's Chesapeake Bay Program (CBP). All sampling sites are located near a USGS stream gage and have a nearby bridge from which high flow samples may be obtained. Most sites are located at the outlet of major basins and represent watersheds with relatively high loads of nutrients and sediments whereas some other sites represent smaller forested or urbanimpacted watersheds.

Pennsylvania's network was created as part of a coordinated effort, conducted by the Chesapeake Bay Program's Non-tidal Workgroup, to include all of the Chesapeake Bay watershed states in a network of stations with comparable collection and analysis protocols. Data from the Non-tidal Network is used to estimate nutrient and sediment loads and trends in concentration for watershed management assessment purposes and for input to the CBP Watershed Model.

Quality Assurance Project Plan Scope. While Pennsylvania's portion of the CBP NTN is 36 stations, this Quality Assurance Project Plan addresses only those 34 PA-DEP (Pennsylvania and New York) sites monitored under its funding agreement with EPA-CBP and two additional sites that are not included in the CBP-NTN (but are completely sampled and analyzed by the same collectors under the same CBP-NTN water and storm sampling protocols)

QUALITY ASSURANCE PROJECT PLAN DOCUMENTATION

- 1. **Project Name:** Chesapeake Bay Non-Tidal Network Water Quality Monitoring (Chesapeake Bay Non-Tidal Monitoring Subset)
- 2. Project Requested By: PADEP Bureau of Clean Water /EPA Chesapeake Bay Grant Conditions

3. Date of Request: 2018 Survey Year

4. Date of Project Initiation: July 2010; revised July 2018

5. Project Officer: Mark Brickner

6. Quality Assurance Officer: Molly Pulket

CHESAPEAKE BAY NON-TIDAL NETWORK PROJECT

7. Project Description:

- A. Objective and Scope Statement: The objectives of the Chesapeake Bay non-tidal monitoring network (CB-NTN) is to build upon Pennsylvania's existing fixed station ambient water quality monitoring network (PA-WQN) activities to include water quality measurements critical to the Bay's restoration programs. Goals of the PA-WQN's CB-NTN component include the establishment and maintenance of a database to support the following monitoring and data quality objectives:
 - Collect ambient and storm sample data at the CB-NTN stations to allow characterization of nutrients and sediments, total nitrogen, phosphorus and suspended sediment from tributary strategy basins;
 - II. Assess the status and trends of nutrient and sediment concentrations and loads at each station by:
 - a. accurately sampling stream conditions under the range of flow conditions during a given year and
 - b. obtaining samples that are representative of stream conditions;
 - III. Compare concentration data and loadings estimates among rivers;
 - IV. Improve calibration and verification of partners' watershed models;
 - V. Assist in describing general water quality conditions and identifying problem areas in Pennsylvania's portion of the Chesapeake Bay basin;

- VI. Identify long-term trends of improvement or degradation in Pennsylvania's portion of the Chesapeake Bay basin;
- VII. Provide a basis for evaluating the success of water quality management in Pennsylvania's portion of the Chesapeake Bay basin.
- **B. Data Usage:** PA-WQN chemistry data are paired with stream discharge information and evaluated to support the goals listed in 7A as follows:
 - I. Basic statistics are calculated (mean, median, standard deviation, etc.) with or without adjustments for flow or season (as determined by evaluation of the data set) to generally characterize water quality by station. These values can be compared to established in-stream criteria to identify water quality problem areas.
 - II. Seasonally adjusted Kendall tests are applied to historic PA-WQN data to assess long-term trends in water quality. When sufficient data exist for flows and chemistry, trend analysis is performed using data plots and the seasonally adjusted Kendall tests or other methods as described in U.S. EPA "Methodologies for Determining Trends in Water Quality Data." These methods are used to describe water quality changes more subtle than those noted in I above. Annual biological collections at PA-WQN stations are analyzed using indices of community structure and composition, ordination, clustering, and professional judgment. The biological community is exposed to the cumulative impact of the water quality and is also a good indicator of water quality trends.
 - III. Collection of data at "ambient" stations provides a measure of background conditions at unaffected or minimally affected sampling locations. These data provide both a measure of long-term water quality trends resulting from airborne contaminants and background water quality as identified by ecoregion. This information can then be used to calculate effluent limits in the permitting program or to determine the potential use attainment of nearby streams degraded by anthropogenic inputs.
 - IV. The evaluation of data as described above provides an overview of the effectiveness of the water quality management program with respect to point source and non-point source impacts viewed in the context of both annual and longer term trends. It also provides an indication of changing background conditions which may result from activities beyond the scope of our program but which impact the water quality management program.
- C. Monitoring Network Design and Rationale: Sampling locations are chosen to ensure that data representative of water quality conditions in a given stream reach will be obtained. The primary factor considered in locating the CB-NTN

stations is their close proximity to a continuous stream flow gage so that the water-quality and discharge information are comparable. Other factors include: watershed land uses, volume and chemical characteristics of known point source wastewater discharges, physiographic and demographic conditions that contribute to non-point source problems and stream hydrology. Sample locations are listed in Attachment A. In all water bodies, every effort is made to sample representative, homogeneous water columns that are comparable over time by using equal-width increment (EWI), isokinetic, and depth-integrated sampling techniques (CBP 2017). Further, to function as an integral part of the overall water quality assessment process, most CB-NTN sites are "piggy-backed" on PA's WQN sites where existing sample parameters can supplement the requisite CB-NTN parameters. Any CB-NTN stations added beyond PA's WQN sites are sampled for the combined CB-NTN and PA-WQN parameters. The CB-NTN stations, when located properly, will also serve to monitor long-term trends in waters affected or unaffected by land-use activities.

In order to achieve these goals, CB-NTN loading station locations were chosen to monitor the status of nutrient and sediment concentrations and loads in the major PA tributaries to the Bay following the specific requirements:

- All stream stations are located close enough to a USGS gage to enable the Department to obtain reliable stream discharge information concurrently with water chemistry,
- II. Monitoring of waters whose quality has been irretrievably altered by such things as abandoned acid mine drainage or large impoundments has been minimized. Stations may, however, be located below large population centers or industrial complexes
- III. Major intra-state streams of different drainage area sizes that demonstrate a spectrum of land-use disturbances from such activities as agriculture and urban areas.
- IV. Use of existing sites (that qualify in I-III above) is maximized to preserve the "history of record" and facilitate trend evaluation.
- D. Monitoring Parameters and Their Frequency of Collection: Water samples are collected monthly as laterally composited depth integrated samples on a predetermined schedule. If high discharge occurs during routine monthly sampling, collect the samples on the scheduled date using procedures for storm event sampling, and including a SSC sample (primary stations only). These samples are to be counted as routine, monthly samples and designated as sample type "Routine, Storm-impacted". A routine, storm-impacted event has a rising discharge (cfs) of at least twice that of the pre-storm's average daily discharge. Eight storm-event samples are required per year, preferably with at least one

storm event per quarter to capture seasonal effects. Sampling of larger storm events is preferred, but in dry years smaller discharges of at least twice that of the pre-storm discharge may be sampled. Twenty water samples are collected per year over a range of flow conditions (12 routine + 8 storm flow) for total nitrogen, total phosphorous, ammonium, nitrate, phosphate and total suspended solids analyses.

Storm samples must also include analyses of suspended sediment concentrations, and each quarter, a sand/fine particle size analysis.

Semi-quantitative benthic macroinvertebrate samples are collected annually across a transect or throughout a large portion of the stream riffle to allow for calculation of RBP metrics as well as the compilation of a representative species list. See Table 1, Section 7E for a specific listing of parameters monitored and ATTACHMENT B for a discussion of the chemical and biological sampling protocols and exact sample locations. Except where noted, Standard Methods 21st edition is the reference. All water chemistry samples are cooled to less than or equal to 6°C without freezing and shipped to the laboratory.

E. Parameter Table:

Table 1. Chesapeake Bay Non-Tidal Network Water Quality Monitoring Network Parameters, Methods and Detection Limits for Water Year 2017

LAB	PARAMETER (expected)	LAB METHOD	TEST CODE	FILTER	MDL	Units	Reporting Level (mg/L)	Holding Time
PADEP	TN	SM Method 4500-N.C + EPA 353.2	00600A	N/A	0.05	mg N/L	0.083	28 days
PADEP	TDN	11	00602A	0.45 micron pore size encapsulated filter	0.05	mg N/L	0.25	28 days
PADEP	NH4W	EPA Method 350.1	00610A	N/A	0.01	mg N/L	0.02	28 days
PADEP	NH4F	п	00608A	0.45 micron pore size encapsulated filter	0.01	mg N/L	0.02	28 days
PADEP	NO23W	EPA Method 353.2	00630A	N/A	0.01	mg N/L	0.05	48 hours
PADEP	NO23F	11	00631A	0.45 micron pore size encapsulated filter	0.01	mg N/L	0.05	48 hours

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PADEP	TP	EPA Method 365.1	00665A	N/A	0	mg P/L	0.01	28 days
PADEP	TDP	"	00666A	0.45 micron pore size encapsulated filter	0	mg P/L	0.01	28 days
PADEP	PO4W	11	70507A	N/A	0	mg P/L	0.01	48 hours
PADEP	PO4F	"	" 0.45 micron pore size encapsulated filter		0	mg P/L	0.01	48 hours
PADEP	TSS	USGS Method I-3765-85	Whatman #934- AH glass fiber		N/A	mg/L	5	7 days
PADEP	TDS	USGS (1989). Method I-1750- 85	70300	Standard glass fiber filter without organic binder, 47 mm (pore size?)	N/A	mg/L	5	7 days
USGS KYSL	SSC_TOTAL	ASTM Method D3977-97(B)		Whatman #934- AH glass-fiber crucible filters, 1.5 µm pore size.	N/A	mg/L	0.5	3 months
USGS KYSL	SSC_TOTAL	ASTM Method D3977-97 C		Sample is poured onto a 62 µm sieve into a dish. The coarse (sand) fraction retained on the sieve is transferred, dried at 103 °C for 2-3 hours, and then weighed. The fine fraction passing through the sieve is analyzed by the filtration method, using Whatman #934-AH glass-fiber crucible filters (1.5 µm pore size).	N/A	mg/L	0.5	3 months

USGS KYSL	SSC_%FINE	п		Metal sieve, 62 micron mesh size	N/A	PCT	0.5	3months
PADEP	тос	APHA Method 5310 C	680	N/A	0.03	mg C/L	0.5	28 days
PADEP	TALK	APHA Method 2320 B	410	N/A	N/A	N/A	N/A	14 days
PADEP	HARDNESS	(Ca + Mg) EPA Method 200.7, Rev. 4.4 Plasma – Atomic Emission Spectrometry	900	N/A	N/A	N/A	N/A	24 hours
PADEP	CLW	EPA Method 300.0; Anions by Ion Chromatography	940	Grade 802 filters, 15 cm diameter	0.03	mg CI/L	0.5	28 days

SM: APHA (2002). Standard Methods for the Examination of Water and Wastewater (20th Edition),

EPA: EPA (1993). Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100.

USGS: USGS (1989). Fishman, M.J., and Friedman, L.C., Methods for the determination of inorganic substances in water and fluvial sediments: US Geological Survey Techniques of Water Resources Investigations, book 5, chapter A1, p. 443.

ASTM: ASTM (2002). Standard Test Methods for Determining Sediment Concentration in Water Samples

8 Schedule of Tasks and Products

U.S. Geological Survey and Susquehanna River Basin Commission staff carries out Non-Tidal Network monitoring on an on-going basis throughout the year. Chemical grab samples (using equal-width increment (EWI), isokinetic, and depth-integrated sampling techniques) are collected on a monthly schedule. Biological samples are collected annually between November 1 and April 30 which corresponds with the PADEP special protection sampling window. Laboratory results, stream flow and biological data are submitted periodically through the Water Quality Exchange (WQX) and are available for download on the Water Quality Portal (WQP). Stream flow and biological sampling data are submitted annually and lag approximately 1 year behind the date of collection. Water quality data for the prior Water Year are submitted to the Chesapeake Bay Program no later than March 15.

¹ Filter - Operationally Defined Particulate (Filter), Dissolved (Filtrate), and (Or) Sieve Analysis (Provide Filter or Sieve type (plate or pleated), and effective pore size in microns)

Trend analyses for PA-WQN data are normally to be performed by USGS/SRBC personnel using currently accepted USGS trend analysis techniques used for other Chesapeake Bay Program signatory agencies.

9. Project Organization and Responsibility

The following is a list of key project personnel and their corresponding responsibilities, and an organizational chart is included to better define their relationships:

DEP, SRBC and USGS Staff

- Sample operations

Water Quality Network Coordinator

- Sample QC

DEP Bureau of Laboratories:

Technical Director Chief, Quality Assurance and Safety Laboratory AnalysisLaboratory QC

Data Management Technician

- Data Processing Activities

PA-DEP/CBP-NTN Water Quality Assessment

- Data Processing QC

Collector/CBP-NTN Water Quality Assessment

Database Manager

-Data Quality Review

Project Officer

- Performance Auditing

Water Quality Assessment Database Manager

- Systems Auditing

Chief, Water Quality Monitoring Section

- Overall QA

Chief, Water Quality Monitoring Section

- Overall Project Coordination

10. Data Quality Requirements and Assessments

Accuracy and Precision Assessment: Accuracy is determined by routine laboratory protocol, which requires random spiking of samples as described in the Bureau of Laboratories, Quality Assurance Manual for the PA Department of Environmental Protection, Bureau of Laboratories (Pa DEP 2016). While precision is normally determined by collecting field duplicate samples at the rate of 1 in 20, for NTN purposes, at least two field duplicates should be collected per station per year. Additionally, if sampling crews vary, then at least one field duplicate should be collected per standard analysis code per collector. The acceptance criteria for field duplicates are for their analytical concentrations to be within ± 20% of each other for

most parameters and \pm 30% for TSS and SSC parameters. See Table 2 for data quality information obtained from the laboratory.

The number of samples required to determine a parameter mean and confidence interval for a specified confidence level and accuracy is both site and parameter specific. A generalized statement is inappropriate since the coefficient of variation, a measure of the variability that determines the number of samples required to accurately estimate the mean, can range from 10% to well over 100% for the same parameter at different stations or for different parameters at the same station. This problem is compounded for metal when the majority of samples are reported as less than the detection limit and/or the concentrations are correlated with stream flow.

Experience with PA-WQN data indicates that at least two years of monthly sampling (including flow measurements) is required to accurately define in-stream water quality and a five-year record is needed to test for trends. Some of the more variable parameters may require even more than five years of data to determine mean instream concentrations. However, since the trend test used (seasonal Kendall test of trends) is a non-parametric test that can incorporate flow corrections, the test is valid even for the most variable (large coefficient of variation) parameters. The current sampling schedule (bimonthly for standard, and monthly for reference and bay loading stations) is appropriate since it eliminates the problem of serial correlation, yet provides enough data to develop a Kendall tau score for each month in the years being evaluated. This has proven to provide a better estimate of trends than the approach that considers data by calendar quarter.

Biological collections are semi-quantitative (RBP) and designed to adequately characterize the type of macroinvertebrate community and describe the dominant taxa at each station. In addition, biological samples will be replicated at a rate of 10% of samples collected.

Bias Assessment: In order to determine if samples have been biased by any contamination introduced by sampling equipment, containers, handling, transport, or collector, field blanks are to be collected from each station at a frequency of a minimum of 1 per year. A NTN field blank (FB) is an aliquot of deionized water free of the analytes of interest, which is placed in a sample container in the field and treated as a sample in all respects, including exposure to sampling site conditions, processing, preservation, storage and all analytical procedures. Because a field blank is treated exactly like an environmental sample at the laboratory, it would then include any contamination introduced during laboratory handling and analysis. Currently, a NTN WQ sample is declared biased if the FB parameter concentrations are ≥ 10% than those of the associated WQ samples.

Field blank preparation is required in the field prior to collecting the water-quality samples, by pouring deionized water into the sampler bottle, transferring it to the churn splitter and if applicable, the field filtration apparatus (CBP 201-7). The field investigator will review sample results and note if target parameters are detected in

the field blank and flag samples accordingly. Sample custody procedures (Section 13 of this document) are followed to ensure proper processing.

Field blanks are to be collected during storm and routinely-scheduled events throughout the year to ensure that a variety of flow conditions and seasonal variability of concentrations are well represented.

Data Representativeness: PA-WQN stations are sited to detect the cumulative impacts of major point and non-point source pollutants on water quality. Intrastate watersheds with drainage areas of greater than 200 square miles or major interstate waterways were chosen. This is a nonrandom siting selection and, as such, each PA-WQN station must be analyzed individually for trend analysis.

At NTN sites, depth-integrated chemical grab samples are collected at equal-width, lateral increments and composited. Biological collections for small to large wadable streams and rivers consist of standardized field collection methods that reflect the indigenous macroinvertebrate community. Biological collection for Large non-wadable rivers consist of standardized artificle substrate collections which do not necessarily reflect the indigenous macroinvertebrate community, but do represent the community that could establish itself if that substrate type were available.

Data Comparability: PA-WQN station locations are fixed to minimize variability from physical and distance factors, such as substrate and travel time (associated with decay or loss of a substance from the water column) from a pollution source to the sample location. Seasonal variation is accounted for by sampling at bimonthly (monthly at ambient reference and bay loading stations) intervals and using data evaluations that compare data from the same month of different years. Variation due to flow is reduced by applying flow corrections before statistical evaluations and/or taking the flow into consideration during judgmental evaluations.

Semi-quantitative macroinvertebrate collection, identification and coding techniques are standardized to insure consistency and repeatability and observations of water body and riparian physical characteristics are noted on the field data sheets (ATTACHMENT C). Chemical sampling collection and analysis techniques are also standardized. These data are also coded and uploaded to the Water Quality Portal.

Data Completeness: The following data are collected from each station: water chemistry, semi-quantitative biological data, and physical measurements/observations of riparian land use, stream substrate composition, hydrologic conditions (flow/depth and channel configuration), aquatic habitat, temperature, pH, and dissolved oxygen.

Water quality variables measured at each station are tailored to the needs of that particular station based upon the factors discussed in the Data Representativeness section and the goal of that sampling station. Sampling variability is noted in the "Comments" column of the Active Stations listings in ATTACHMENT B. Trend analysis is performed on the chemical data if five out of ten years of data are available and if the 5 years are relatively uniformly spread over the ten-year period. Biological

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data can be assessed, at least with professional judgment, if two years of data are available.

FIGURE 1
QUALITY ASSURANCE ORGANIZATION CHART

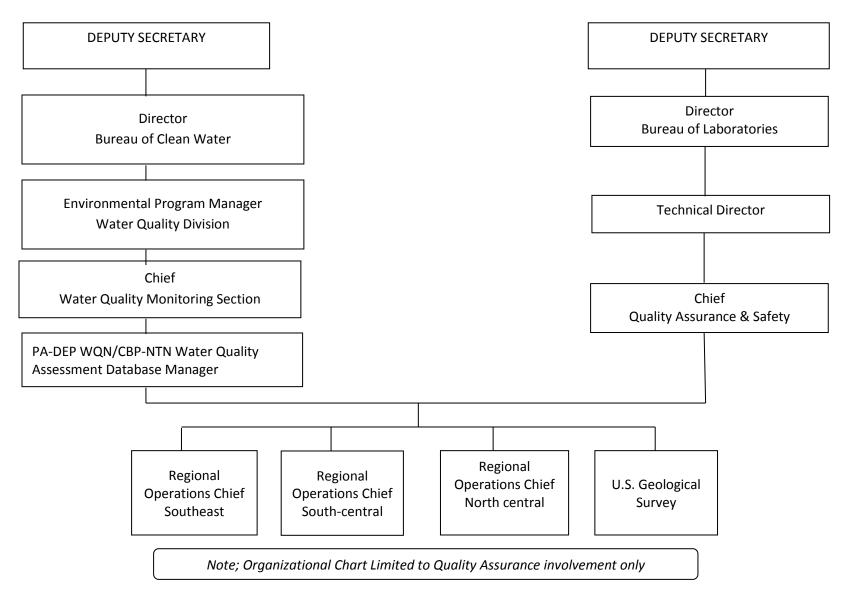


Table 2. Ambient Fixed Station/Water Quality Network Monitoring Parameter Data Quality Assessments

Data Quality Assessments											
STORET	Parameter	Mean Lab Control Value	Mean Percent Recovery ¹	Percent Relative Standard Deviation ²							
00310	Biochemical Oxygen Demand 5 Day	206.0 mg/L	103.1	5.1							
00403*	рН	7.02 pH units	100.24	0.57							
00410*	Alkalinity, Total as CACO3 (Titrimetric)	248 mg/L	99.1	0.9							
00515	Residue, Dissolved at 105° C		Data Not Available								
00530	Total Suspended Solids	94 mg/L	94.4	7.8							
00600A	Nitrogen, Total	4.04 mg/L	101.0	0.15							
00610A	Ammonia, Total as Nitrogen	0.989 mg/L	98.87	1.53							
00615A	Nitrite Nitrogen, Total	0.205 mg/L	102.34	3.24							
00620A	Nitrate as Nitrogen	0.78 mg/L	77.9	3.44							
00625A	Nitrogen, Kjeldahl Total	5.04 mg/L	100.81	2.22							
00602A	Nitrogen, Dissolved	4.05 mg/L	101.2	3.76							
00665A	Phosphorus, Total as P	0.401 mg/L	100.2	4.3							
70507A	Phosphorus, Total, Orthophosphate as P	0.512 mg/L	102.4	3.5							
00680	Carbon, Total Organic	1.94 mg/L	97.2	3.5							
00719A*	Cyanide, Free	19.54 μg/L	97.72	4.40							
00720A*	Cyanide	0.0197 mg/L	98.58	2.79							
00900*	Hardness, Total (Calculated)	13 mg/L	100.00	0.00							
00916A*	Calcium, Total by Trace Elements	5.03 mg/L	100.61	2.26							
00927A*	Magnesium, Total by Trace Elements	5.13 mg/L	102.50	2.25							
00940	Chloride, Ion Chromatography	9.74 mg/L	96.22	1.55							
00945	Sulfate, Ion Chromatography	19.97 mg/L	99.84	4.30							
00951	Fluoride	1.02 mg/L	101.55	1.58							
01042A*	Copper, Total by Trace Elements	204.25 μg/L	102.13	2.33							
01045A*	Iron, Total by Trace Elements	1049.73 μg/L	104.97	2.59							
01055A*	Manganese, Total by Trace Elements	514.50 μg/L	102.90	2.22							
01067H*	Nickel, Total by Trace Elements	206.31 μg/L	103.16	2.62							
01092H*	Zinc, Total by Trace Elements	205.27 μg/L	102.64	2.49							
01105H*	Aluminum, Total by Trace Elements	967.94 μg/L	96.79	2.15							
32730D	Phenols	82.15 μg/L	102.69	4.47							
82079	Turbidity, Nephelometric	4.84 NTU	96.85	6.26							

Time period of data from 1/1/2015 to 7/31/2015, except for parameters noted with * which are from 2010 data.

Completeness will be judged on whether the minimum number of samples can be collected in order to analyze trends. If data is deemed to be incomplete resampling will be required.

Accuracy is considered acceptable and meeting established criteria when within + or - 20 percent of a known (80-120 percent recovery). Percent Recovery is calculated from the mean analyte recovered for the period, divided by the lab control value. Standard Deviation for the period of observation is calculated in Microsoft Excel using spreadsheet functions for standard deviation and mean.

Standard Deviation

S.D. =
$$\sqrt{\frac{\sum_{s=1}^{m} \sum_{i=1}^{n} (y_{is} - M)^{2}}{(n_{y} - 1)}}$$

$$M = \frac{\sum_{s=1}^{m} \sum_{i=1}^{n} y_{is}}{n_{y}}$$

where:

s = series number

i = point number in series s

m = number of series for point y in chart

n = number of points in each series

 y_{is} = data value of series s and the ith point

 n_y = total number of data values in all series

M = arithmetic mean

Standard Error

$$S.E. = \sqrt{\frac{\sum_{y=1}^{m} \sum_{i=1}^{n} y_{is}^{2}}{(n_{y} - 1)((n_{y}))}}$$

11. Sampling Procedures

Section B (CBP 2017) describes the sampling procedures to be followed when collecting for CBP-NTN samples. As most of the CBP-NTN stations are "built on" PA-DEP WQN sites, Section B procedures are compatible with the sampling procedures referenced for these PA-DEP sites (DEP 2012 & USGS 2012). Consequentially, all CBP-NTN field collections will be made in accordance with the Bureau of Clean Water's WQN (DEP 2012 & USGS 2012) and Water Quality Monitoring Protocols for Streams and Rivers (DEP 2018) field procedures and USGS stream gauging techniques.

Consistent adherence to CBP 2017 sampling procedures by CBP-NTN field crews is critically important because of the data quality assurance these methods provide.

Significant components of the CBP 2017 sampling procedures include the use of depth-integrating samplers, churn splitters, and "clean hands" sample processing procedures. The integrating samples are deployed incrementally across stream cross-sections to assure that a continuous sample of the water column is collected at each stream cross-section increment. The churn splitters are used to composite and mix the collected increment aliquots. In order to avoid sample contamination, a "clean hands" sample equipment and bottle procedure is followed by preparing a clean work area to process the collected samples and one person dedicated to handle the churn, reagents, and sample bottles with new, unused disposable powderless gloves.

¹Percent Recovery estimated from the recovery of pure material spiked into deionized water.

²Standard Deviation calculated from a minimum of three months of laboratory quality control data for calibration check standards.

12. Sample Custody Procedures

Samples collected in the field are identified by date, time, place, and survey name and are accompanied by a Request for Chemical Analysis Form. Both the form and sample container bear a unique 7 digit identifying number and are transported together (in a shipping cooler filled with ice) to the DEP Bureau of Laboratories in Harrisburg via contracted courier service.

13. Calibration Procedures and Preventive Maintenance

Meter calibration should be accomplished at the beginning of each sampling effort in accordance with the manufacturer's recommendations. In the case of pH and specific conductance, this is accomplished using a reference standard. Calibration checks should be performed throughout the day if multiple samples will be collected. Results of calibration and the performance of preventative maintenance recommended by the manufacturer must be recorded in an equipment logbook maintained for each piece of equipment. Dates of equipment use, calibration results and operator maintenance activities must be recorded.

14. Documentation, Data Reduction, and Reporting

- A. Documentation: Field data is recorded on prescribed field forms (see AttachmentsC?). The biologist responsible for the survey reviews the field forms for completeness and legibility at the completion of each survey. The results of laboratory biological identification are recorded on prescribed forms and initialed by the taxonomist. Field forms and notes, taxonomic forms, survey maps, correspondence, and all other pertinent information are kept in coded water body files maintained by the Bureau of Clean Water.
- B. Data Reduction and Reporting: Coded field and laboratory data are transferred to a standard computer database. After the entry is complete, the Water Quality Network Coordinator reviews a listing of the data for accuracy and completeness. Data is then transferred to the EPA Water Quality Portal and the data entry clerk confirms data accuracy and completeness. Analyses of trends at select PA-WQN stations are published biennially in DEP's Integrated Water Quality Monitoring and Assessment Report (Integrated Report) available on DEP's Web site. Regarding CBP-NTN data, it is submitted annually to the Chesapeake Bay Program using the Data Upload and Evaluation Tool (DUET). Prior to submission, the NTN station information and data is checked for completeness in a DEP Oracle database. The data is downloaded into an Access database where multiple queries are run to check and format the data. Consistency checks are run and the data is coded where applicable.

15. Data Peer Review

The protocol for data peer review of chemical data is found in the Quality Assurance Manual for the PA Department of Environmental Protection, Bureau of Laboratories (Pa DEP 2010). Laboratory external quality assessments are performed on a bi-annual basis for the NELAP Institute by the New Jersey Department of Environmental Protection. This review includes a thorough review and evaluation of laboratory standard operation procedures prior to the onsite visit and observation and questioning of staff during the site visit. It also includes a directed review of laboratory data. Internal audits are performed annually by the Bureau of Laboratories and these audits include peer review of data. A log is maintained of field instrumentation calibrations, performance and repairs. Taxonomy of questionable organisms is verified by cross checking with other taxonomists. Database fields are validated through error checking routines and automatic exclusion of data outside of specified ranges. Records of analyses used in the assessment of survey data are maintained in the water body file. At a minimum, this includes a copy of the data used in the analytical program, a copy of the analytical program, the program output, normality testing (if parametric tests are used), and a rationale for eliminating outliers or creating data subsets. The outputs shall be initialed and dated by the analyst.

16. Performance and Systems Audits

The PA-WQN Coordinator checks field staff for adherence to protocols and also audits, at random, stream files to verify that data documentation is accurate and complete, and that appropriate analytical techniques are used. The PA-WQN Coordinator will maintain records for each individual to include: (1) date of audit; (2) a list of protocols for which the individual was evaluated; and (3) any deficiencies noted.

17. Corrective Action

The Bureau of Laboratories, data entry clerk, the taxonomist, in-house review of reports, and audits detect errors through verification of data. When problems are noted, the individual is notified, provided with the appropriate protocol and training, and reevaluated before performing the task again. The auditor shall maintain the records of any corrective actions on the Department's Employee performance evaluation system.

18. Reports

Reports concerning ongoing performance and systems audits, data quality assessments, and significant quality assurance problems will be included in the semi-annual grant status report to EPA and will be provided to the Department's Quality Systems Program Manager and the Chief of the Water Quality Division. Results of trend analyses of PAWQN data are documented in the Integrated Report and annual updates.

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- Chesapeake Bay Program 2017. Chapter 5, Nontidal Water Quality Monitoring. https://www.chesapeakebay.net/documents/CBPMethodsManualMay2017.pdf
- Department of Environmental Protection. 2018. <u>Water Quality Monitoring Protocols for Streams and Rivers</u>.
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- United States Geological Survey. 2012. <u>Pennsylvania's Statewide Water Quality Network Sampling Procedures and Protocols</u>. (a joint USGS and PA-DEP unpublished file document; 4/16/2014 edits)

Attachment A Station Locations

WQN	STATION NAME	COLLECTOR	LOCATION	MUNICIPALITY	COUNTY	LATITUDE	LONGITUDE	USGS GAUGE	GAUGE LOCATION	DRAIN AREA (SQ MI)
201	Susquehanna Rvr @ Marietta	SRBC	SR462 BR	HEMPFIELD TWP	LANCASTER	40.028100	-76.519000	01576000	420' UPSTR FR CHICKIES CRK - MARIETTA	25990
204	Pequea Crk	SRBC	SR 324 Br @ Martic Forge	CONESTOGA TWP	LANCASTER	39.905700	-76.328314	01576787	SR324 BR - MARTIC FORGE	148
210	W Conewago Crk	SRBC	SR181 BR	NEWBERRY TWP	YORK	40.081400	-76.718000	01574000	500' UPSTR FR SR181 BR - MANCHESTER	510
214	Juniata Rvr	SRBC	SR34 BR	NEWPORT	PERRY	40.479030	-77.128130	01567000	DWNSTR SIDE OF SR34 BR - NEWPORT	3354
223	Raystown Br Juniata	SRBC	SR913 BR W OF SAXON	LIBERTY TWP	BEDFORD	40.215012	-78.264872	01562000	500' DWNSTR FR SR913 BR - SAXTON	756
226	Mahantango Crk	SRBC	S Malta Rd (T482) Bridge	Upper Paxton Twp	Dauphin	40.611111	-76.911520	01555500	2.0 mi upstrm from mouth - East Mahantango Crk Nr Dalmatia	162.5
229	Penns Crk	SRBC	SR104 BR - VILLAGE OF PENNS CRK	CENTRE TWP	SNYDER	40.867000	-77.049270	01555000	200' DWNSTR FR SR104 BR - PENNS CREEK	301
243	Sherman Crk	SRBC	PISGAH STATE RD CROSSING @ DROMGOLD	CARROLL TWP	PERRY	40.344200	-77.194350	01568000	SR 34 BRIDGE - SHERMANSDALE	207
259	Muddy Crk	USGS	upstrm of SR 2024 (Paper Mill Rd) bridge	Peach Bottom Twp	York	39.773020	-76.316200	01577500	upstrm of the SR2024 Br - Castle Fin	132.8
263	Octoraro Crk	SRBC	US 1 @ Richardsmere, MD	RICHARDSME RE, MD	CECIL	39.693683	-76.124727	01578475	NEW BRIDGE ROAD BRIDGE NEAR RICHARDSMERE, MD	189.2
271	Conodoguinet Crk	SRBC	SAMPLE ROAD BRIDGE	SILVER SPRING TWP	CUMBERLAND	40.255455	-77.018537	01570000	1000 FT UPST OF TR 596 - HOGESTOWN	470
272	Swatara Crk	SRBC	JUST UPSTRM OF HANOVER ST BR @ SWATARA CRK PARK	DERRY TWP	DAUPHIN	40.287170	-76.677800	01573560	0.5 MI UPST OF SR 39 - HERSHEY	485
273	Conestoga Rvr	SRBC	RIVER ROAD BRIDGE (SR 3030) @ SAFE HARBOR	MANOR TWP	LANCASTER	39.939120	-76.387370	01576754	SR 3030 BRIDGE	470

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									07/03/2016	
WQN	STATION NAME	COLLECTOR	LOCATION	MUNICIPALITY	COUNTY	LATITUDE	LONGITUDE	USGS GAUGE	GAUGE LOCATION	DRAIN AREA (SQ MI)
281	Paxton Crk	SRBC	Kohn Road crossing; 0.5 mi dwnstrm of Progress Ave	Susquehanna Twp	Dauphin	40.306099	-76.855639	01571000	Progress Ave - near Penbrook, PA	11.6
282	Kishacoquillas Crk	SRBC	Bridge on Manns Narrows Rd	DERRY TWP	Mifflin	40.654581	-77.583589	01565000	150 ft dwnstrm from Br on old US Hwy 322 - Reedsville	163
284	Pequea Crk	USGS	S Ronks Rd	Strasburg Twp	Lancaster	40.009167	-76.162222	01576767	Pequea Creek near Ronks, PA	70
285	Quittapahilla	USGS	Palmyra- Bellgrove Rd	N Annville Twp	Lebanon	40.342389	-76.561104	01573160	Palmyra Bellegrove Rd - NR Bellegrove PA	74.2
286	Codorus Creek	USGS	Codorus Furnace Rd (SR 1008)	E Manchester Twp	York	40.052256	-76.654454	01575585	PA 24 Br - Codorus Creek at Pleasureville, PA	276.8
301	Susquehanna Rvr - Danville	SRBC	SR54 BR	MAHONING TWP	MONTOUR	40.957700	-76.621200	01540500	200' UPSTR FR MILL ST BR ON SR54 - DANVILLE	11220
302	Susquehanna Rvr - Wilkes-Barre	SRBC	BR EAST OF US RT 11 NR RETREAT STATE PRISON	NEWPORT TWP	LUZERNE	41.189000	-76.087200	01536500	DWNSTR SIDE OF NORTH ST BR - WILKES-BARRE	9960
305	Susquehanna Rvr - Towanda	SRBC	James Street bridge	Wysox Twp	BRADFORD	41.791592	-76.442914	01531500	BRIDGE ST - TOWANDA	7797
401	W Br Susquehanna Rvr - Lewisburg	SRBC	SR45 BR	LEWISBURG	UNION	40.966903	-76.878719	01553500	MARKET ST BR ON SR45 - LEWISBURG	6847
404	W Br Susquehanna Rvr - Karthaus	SRBC	SR 879 BRIDGE @ KARTHAUS	KARTHAUS TWP	CLEARFIELD	41.116950	-78.109140	01542500	900 FT UPST OF SR 879 BRIDGE - KARTHAUS	1462
445	Bald Eagle Crk	SRBC	SR2012 (LR18013) BR - CASTANEA	CASTANEA TWP	CLINTON	41.124629	-77.435039	01548005(D) 01548085(WW)	BALD EAGLE CREEK NEAR BEECH CREEK STATION, PA	768
448	W Br Susquehanna Rvr - Jersey Shore	SRBC	SR 44 BRIDGE @JERSEY SHORE	JERSEY SHORE BORO	LYCOMING	41.202447	-77.252190	01549760	SR 44 BRIDGE - JERSEY SHORE	5225
462	Chillisquaque Crk	USGS	Shakespeare Rd (SR1025)	E Chillisquaque Twp	Northumberland	40.974586	-76.800122	01553850	Chillisquaque Crk near Potts Grove, PA	101.2
212	Yellow Breeches	USGS	BRIDGE ST BR (OLD US RT 11) - NEW CUMBERLAN D	FAIRVIEW TWP	YORK	40.224186	-76.860560	01571500	150' DNSTR FR OLMSTED MILL DAM - CAMP HILL	216

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WQN	STATION NAME	COLLECTOR	LOCATION	MUNICIPALITY	COUNTY	LATITUDE	LONGITUDE	USGS GAUGE	GAUGE LOCATION	DRAIN AREA (SQ MI)
217	Little Juniata Rvr	USGS	SR45 Br	Spruce Creek Twp	Huntingdon	40.609059	-78.136330	01558000	150' dwnstr from Penn Central R&R br - Spruce Crk	220
224	Frankstown Br Juniata	USGS	abandon R&R Br 0.6 RM upstrm of Clover Crk; off SR2013	Woodbury Twp	Blair	40.471857	-78.186795	01556000	10' dwnstr from SR2015 Br - Williamsburg	291
269	Conewago Crk - Falmouth	USGS	300 yards downstr of Hillsdale Rd bridge	Conoy Twp	Lancaster	40.15111	-76.68974	01573710	Conewago Crk near Falmouth, PA	47.3
278	Conewago Crk - Bellaire	USGS	Prospect Rd crossing NR Lebanon/Lanc aster County Border	Mount Joy Twp	LANCASTER	40.195277	-76.567777	01573695	Conewago Crk near Bellaire, PA	20.5
280	Big Spring Run	USGS	Along Gypsy Hill Rd about 0.4 miles from US 222	West Lampeter	Lancaster	39.995833	-76.263888	015765195	Big Spring Run NR Mylan Corners, PA	1.68
317	Tunkhannock Crk	USGS	SR6 BR	TUNKHANNOC K TWP	WYOMING	41.557248	-75.894432	01534000	300' UPSTR FR US HWY 6 BR @ DIXON - TUNKHANNOCK	383
410	Pine Crk - Waterville	USGS	900 ft dwnst of gage, just upstr of island; along Rt 44	CUMMINGS TWP	LYCOMING	41.272175	-77.326953	01549700	.9 MI DWNSTR FR RAMSEY RUN - WATERVILLE	944

The two stations below are not officially part of Pa-DEP's CBP-NTN but are PA-WQN stations that have been activated or upgraded for other water quality purposes. However, the analytical requirements of these two stations are the same as for CBP-NTN stations. Since the data collected from WQN 202 and 203 are the same as collected at the CBP-NTN stations (storm events included), employs the same collectors, and same CBP-NTN water and storm sampling protocols, it is provided to CBP as part of PA-DEP's DUET data transfer.

WQN	STATION NAME	COLLECTOR	LOCATION	MUNICIPALITY	COUNTY	LAT	LONG	USGS GAUGE	GAUGE LOCATION	DRAIN AREA (SQ MI)
202	Susquehanna Rvr @ Hburg	USGS	Market Street Bridge	Harrisburg	Dauphin	40.2566	-76.88465	01570500	60 ft dwnstr from Market St Bridge - E bank of City Island - Harrisburg	24083
203	Susquehanna Rvr @ Sunbury	USGS	VETERANS MEMORIAL BR BTWN SUNBURY & SHAMOKIN DAM; ST HWY 61	UPPER AUGUSTA	NORTHUMBERL AND	40.8515	-76.807088	01554000	AT PP&L GENERATING PLANT - SUNBURY	18300

ATTACHMENT B

2016 Pennsylvania Integrated Water Quality Monitoring and Assessment Report

http://www.dep.pa.gov/Business/Water/CleanWater/WaterQuality/Integrated%20Water %20Quality%20Report-2016/Pages/default.aspx

ATTACHMENT C FLOWING WATERBODY FIELD FORM



COMMONWEALTH OF PENNSYLVANIA DEPARTMENT OF ENVIRONMENTAL PROTECTION BUREAU OF WATER STANDARDS AND FACILITY REGULATION

FLOWING WATERBODY FIELD DATA FORM

(Information and comments for fields boxed in double lines are required database entries. Other fields are optional for personal use.)

Date-Time Exar		*	-		-	Sta	te Water Plan	Stre		Ch. 93 Use		
20040212-	0312-XYZ	Date		Time	Initials							
Secondary ID	Station					Surve	yed					
*Date as YYYYMMDD, time as military time, and your initials uniquely identify the stream reach.												
Survey Type												
(1) Basin Survey, (2) Cause / Effect, (3) Fish Tissue, (4) Intensive Surface Waters Assessment (UW) Follow-up, (5) Point-of-First-Use, (6) SERA, (7) Antidegradation (Special Protection), (8) Toxics, (10) Use Attainability, (11) WQN												
Location												
County:					Munic	ipality:						
Location De	scription:											
					Land Use							
Residential:		% Comme	cial:	%	Industrial:	%	Cropland	d: %	Pasture:	: %		
Abd. Mining: Land Use Co		% Old Field	ds:	%	Forest:	%	Other:	%				
Canopy cov	er: 🗌 o	pen 🗌	partly sha	ded	☐ mostly sl	naded	full	y shaded				
				1	Water Quality	•						
Habitat evalua	ated?	Yes (score _ No)		eam type:	estone (c	old/warm)	☐ limesto	ne 🗌 li	imestone-		
Flow measur	ement tak	en: Yes	□No									
			Field Mete	Readir				otes (N-norn				
	ector- ence #	Temp (°C)	DO (mg/L)	рН	Cond. (umhos)	filt	ered, MF-	metals filtere indicate		t, Others:		
1.			(3, -/		()				,			
2. 3.												
<u> </u>			<u> </u>		Findings							
Not		Impaired		Impaire	ed 🗆	Is imp			evaluate			
Impaired: biology? habitat? localized? designated use? Decision comments. Describe the rationale for your "Not Impaired" or "Impaired" decision; reach locations for use												
designation reevaluations; special condition comments; etc.:												
					age netroleum (ath an' M	-10				

Common descriptors: Water Odors - none, normal, sewage, petroleum, chemical, other; Water Surface Oils - none, slick, sheen, globs, flecks; Turbidity - clear, slight, turbid, opaque; NPS Pollution - no evidence, some potential, obvious; Sediment Odors - none, normal, sewage, petroleum, chemical, anaerobic; Sediment Oils - absent, slight, moderate, profuse; Deposits - none, sludge, sawdust, paper fiber, sand, relict shells, other. Are the undersides of stones deeply embedded black?

AQUATIC BIOTA (general)											
Periphyton*: Filamentous Algae											
* Relative Abundance (RA): (0 = absent, R = rare ** For more detailed macroinvertebrate surveys, us	, P = present, C = common, A = abundant, VA = very abundant se Unassessed Waters form (pg. 2) for RA data; for fish, use the) e section below)									
Preserved Macroinvertebrate Sample	?										
Sampling method: Std. kick screen:	D-frame: Surber: Other:	method?:	<u> </u>								
FISHERIES DATA											
Sampling Duration (min): Distance (m):, Widths (m):, = (avg.) Area (m²):											
	nt good fair poor ver	ry poor									
	□ bank full □ moderate □ flow	C									
	Gear Used:		ent (AC/DC):								
Gear/Crew Performance/Comments: _											
Preserved Fish Sample ?	☐ Yes ☐ No Label ID, if yes:										
Genus/Species	Adults	Juveniles	Anomalies								
	_										
	Commonto/Ab.undonos Notes										
Comments/Abundance Notes:											
Comments:											

ATTACHMENT D

Pennsylvania's Statewide Water Quality Network Sampling Procedures and Protocols

(& Appendix A: U. S. Geological Survey Surface-Water Quality Field Form)

United States Geological Survey
PA Department of Environmental Protection

WQN Surface-Water Chemistry Sampling

Teams from each of the four Pennsylvania USGS offices (Exton, New Cumberland, Williamsport and Pittsburgh) will conduct surface-water chemistry sampling. For purposes of this document, the term "team" refers to the individual or individuals from each office who has been directed to conduct the sampling, any assistants who have been assigned and backup personnel who have been trained to conduct the sampling in the event the primary individual(s) cannot conduct the sample collection. The sampling will be conducted by a single individual, with the following exceptions: requirements of the bridge-safety plan, requirements of the cableway operation, and other occasions such as extreme high flow, where a single individual cannot safely collect the sample.

Each team member should have access to the following two documents: PADEP Pennsylvania's Surface Water Quality Monitoring Network (PSWQN) and the USGS National Field Manual for the Collection of Water-Quality Data (NFM). Both of these manuals will be referenced throughout the remainder of this document.

For your reference, the USGS National Field Manual for the Collection of Water-Quality Data contains the following chapters:

- A1 Preparations for Water Sampling
- A2 Selection of Equipment for Water Sampling
- A3 Cleaning of Equipment for Water Sampling
- A4 Collection of Water Samples
- A5 Processing of Water Samples
- A6 Field Measurements
- A7 Biological Indicators
- A8 Bottom-Material Samples
- A9 Safety in Field Activities

Sampling Equipment

The following equipment will be used in the collection of samples for the water-quality network project. Equipment will be maintained by the sampling crews and replaced or upgraded as necessary.

Multi-parameter water-quality meters will be available to each sampling team. Each set should also include a back-up meter or individual meters. Meters will have the capability to measure dissolved oxygen, pH, specific conductance and temperature. Calibration will be conducted daily, and recorded in a logbook. The calibration standards to be used will be based on historical water-quality data from the site(s) that are to be sampled that day. For instance, if you are planning on sampling a site that typically has a pH value that ranges between 7.3-7.7, a two-point calibration should be performed with pH standards 7 and 10.

Sample collection devices include the DH-81 wading sampler, the US-WBH-96 weighted-bottle sampler, and the DH-95 bridge sampler. Determination of the appropriate sampling device, along with proper techniques to be used at each site, is discussed in *Surface Water Sample Collection Section*.

A bridge crane and reel assembly will be available to each team to use for bridge samples (instructions for maintenance of the B-reel can be found in Technical Information Sheet for Servicing of the USGS Sounding Reel, March 1989).

A 4, 8, or 14 L plastic churn splitter will be used to split samples.

A 0.45 μ m capsule filter will be used to filter samples for the determination of dissolved constituents. The sample will be pumped through the filter using a peristaltic pump, hand pump, or squeeze bottle and a cleaned length of silicon tubing.

Field Equipment Checklist

- 1. USGS National Field Manual for the Collection of Water-Quality Data
- 2. PADEP Pennsylvania's Surface Water Quality Monitoring Network manual
- 3. Sampling equipment
 - a. DH-81
 - b. Weighted bottle sampler (US-WBH-96)
 - c. DH-95
 - d. Bridge crane & reel
 - e. Churn splitter (8-liter, 14-liter)
 - f. 1-liter bottles (wide mouth & narrow mouth)
- 4. Sample bottles
 - a. 500 ml plastic bottles (clear cap)
 - b. 500 ml glass bottle (white lid)
 - c. 125 ml plastic bottles (blue cap)
 - d. 125 ml plastic Bacteria bottle (blue cap)
- 5. Acid preservatives
 - a. Sulfuric acid (5 ml, 1:9 N)
 - b. Nitric acid (2 ml, 1:1 N)
 - c. Sodium hydroxide (5 ml, 2.5 N)
- 6. Capsule filters (0.45 um)
- 7. Clean silicon tubing
- 8. Peristaltic pump
- 9. 12-V battery
- 10. Discharge measurement equipment (wading rod, velocity meters, tag-line, steel tape, stopwatch, headphones, current meter digitizer, Aquacalc, measurement sheets)
- 11. Field forms (USGS & PADEP)
- 12. Field book (to track & record specific information relative to each collected sample e.g., WQN #, Sequence #, Date and Time, field parameters)
- 13. Water-quality meters
- 14. Calibration standards & logbook
- 15. Cellular phone
- 16. PA Gazetteer
- 17. PADEP's courier service bills of lading
- 18. Field folders containing the following:
 - a. Directions to QW site and USGS gage
 - b. Digital camera & photos of site
 - c. Job Hazard Analyses (JHAs)
 - d. Traffic Safety Plans (TSPs)

Field Equipment Checklist Cont.

- 19. PADEP coolers w/ ice
- 20. Cleaning supplies (tap water, DIW, non-phosphate detergent mix, acid rinse)
- 21. Safety equipment
 - a. Flotation device (pfd, float coat)
 - b. Hip-boots
 - c. Chest waders
 - d. Orange safety vest
 - e. USGS visual identity (hat, t-shirt, sweatshirt)
- 22. Nitrile gloves
- 23. Travel forms
- 24. Litmus strips
- 25. Aluminum foil (to wrap around the Phenol bottle)
- 26. Baking soda (to neutralize the used acid rinse water)

Surface Water Sample Collection

Surface water samples are collected monthly at reference, standard monthly, and CBP Loading sites and bimonthly at standard sites. The samples should also be at least 3 weeks apart if possible. The sampling months for standard sites are changed each water year to assure random sampling. Odd numbered months are sampled in odd numbered water years and even numbered months are sampled in even numbered water years. New set of reference sites are selected every five years. Surface water samples will be collected, to the extent possible, in accordance with the NFM; exceptions to this policy will be noted herein.

Samples are collected using the Equal-Width-Increment Method (NFM, chapter A4). One of the following depth-integrating vertical samplers will be utilized to collect samples at all sites unless the velocity of the stream is < 1.5 ft/s, which is the minimum velocity requirement for an isokinetic sample. The sample collection devices and methods are: DH-81 wading sample, weighted-bottle sampler (US-WBH-96) with rope, and the DH-95 with bridge crane. Selection of the appropriate sampling device/method is based on flow conditions, safety, and the type of sample being collected. Limitations of these samplers are summarized in Table 2.2 of the NFM. While collecting an isokinetic sample, an appropriate transit rate (the rate at which the sampler is lowered or raised) should be utilized. Additional information with regard to transit rates is available in Chapter A4 of NFM.

An exception to collecting an isokinetic sample is when the velocity of the stream is < 1.5 ft/s. In this case, it is acceptable to obtain grab samples with an open bottle.

Samples will be collected in pre-cleaned 1-Liter plastic bottles and composited in a pre-cleaned churn splitter. The number of verticals sampled will be based on the stream width and mixing conditions (Table 1). An odd number of vertical samples will be collected. The purpose being that when water-quality parameters, such as pH, temperature, specific conductance, dissolved oxygen are being collected/recorded at each vertical, a median value will ultimately be available. These median values will be associated with the sample and recorded on the field sheets, lab sheets, and entered into the database. The usefulness of a median value is that it is an actual value and not an average value. USGS sampling teams are directed to document the horizontal QW profile of the streams once a year to determine the adequacy of the number of verticals, and recommend changes in the number of verticals

if necessary. It is important to be able to ascertain the natural mixing capabilities of a stream, and the horizontal profile will help determine this characteristic.

The following guidelines regarding the number of verticals are to be used at all sites. If the QW profile indicates incomplete mixing conditions then additional verticals may be needed.

Table 1: Minimum number of sampling verticals based on stream width.

Width of Waterway (ft.)	Minimum # of Verticals
<u>0-25</u>	<u>1</u>
<u>25-100</u>	3
100-250	<u>5</u>
250-500	7
<u>>500</u>	9

Field rinsing of the churn splitter and sample collection bottle consists of pouring 2 to 4 L of native sample water into the churn and then vigorously swirling the water inside the churn and moving the churn disk up and down. The rinse water should then be drained from the churn via the spigot and pouring it out through the top of the churn.

Samples will be composited in a churn splitter (4, 8 or 14 liter) until sufficient water has been collected for the necessary analyses (and all verticals have been obtained, if applicable). Bottles will be filled from the churn splitter in accordance with the standard analysis code (SAC) (Table 2). The 500-ml plastic bottles should be triple-rinsed with sample water from the churn splitter prior to filling. Nitrile gloves should be worn while rinsing, filling, and preserving all sample bottles. Information on each SAC code is listed in Table 3.

Table 2: Standard analysis codes and bottle sets

	Standard Inorganics	Special Inorganics	тос	DOC	Total Metals	Dissolved Metals	Na & K	Dissolved Standard	Dissolved Nutrients	Radio- logical	Bacterio- logical
Standard Analysis Code (SAC)	500 ml plastic bottle unfiltered unfixed	500 ml plastic bottle unfiltered fixed H2SO4	40 ml amber VOA vials unfiltered fixed H2SO4	40 ml amber VOA vials filtered fixed H2SO4	125 ml plastic bottle unfiltered fixed HNO3	125 ml plastic bottle Filtered fixed HNO3	125 ml plastic bottle unfiltered fixed HNO3	125 ml plastic bottle Filtered unfixed	125 ml plastic bottle Filtered fixed H2SO4	500 ml plastic bottle unfiltered unfixed	Sterilized 125 ml plastic, blue cap bottles unfiltered unfixed
010	2	1			1						
012*	3	1	2		1			1	1		
013	3	1			1	1					1
015	3	1	2		1	1					1
016	3	1			1	1					
021				2			1				
121				2			1				
610	2	1			1						
612*	3	1	2		1			1	1		
616	3	1			1	1					
RAD99										2	

Table 3. Pennsylvania Water Quality Network Standard Analysis Code Parameters

	Stand	ard WQN	Bay Loading WQN		Reference	Ambient WQN	Low Alk	BLM	
	Routine	+ Marcellus	Routine		Routine	low alkalinty	Routine	+ Marcellus	WQN
Statndard Analysis Codes>	242	242	040	242	242	045	242	040	204
Parameters (total)	010	610	012	612	013	015	016	616	021
Specific Cond - SC	Х	Х	Х	Х	Х	Х	Х	Х	-
pH (Lab)	Х	Х	Х	Х	Х	Х	Х	Х	-
Alkalinity - Alk	Х	Х	Х	Х	Х	Х	Х	Х	-
Total Susp Sol - TSS	Х	Х	Х	Х	Х	Х	Х	Х	-
Nitrogen - N	Х	Х	X + diss	X + diss	Χ	Х	Х	Х	-
Ammonia - NH3	Х	Х	X + diss	X + diss	Х	Х	Х	Х	-
Nitrite - NO2	Х	Х	-	-	Х	Х	Х	Х	-
Nitrate - NO3	Х	X	-	-	Х	Х	Χ	Х	-
Nitrate+Nitrite - NO3+NO2	•	-	X + diss	X + diss	-	-	-	1	-
Phosphorus - P	Х	Х	X + diss	X + diss	Х	Х	Х	X	-
Phos-Ortho - P-ortho	Х	Х	X + diss	X + diss	Х	Х	Χ	X	-
Hardness - Hardness	Х	X	Χ	Х	Χ	Х	Χ	Х	-
Calcium - Ca	Х	X	Х	X	Х	X + diss	X + diss	X + diss	-
Magnesium - Mg	Х	X	Χ	X	Χ	X + diss	X + diss	X + diss	-
Chloride - Cl	Х	X	Х	X	Х	X	Х	X	-
Sulphate - SO4	Х	X	Х	X	Х	Х	Χ	X	-
Copper - Cu	Х	X	Х	X	X + diss	X + diss	X + diss	X + diss	-
Iron - Fe	Х	X	Х	X	X + diss	X + diss	X + diss	X + diss	-
Lead - Pb	X	X	Х	X	X + diss	X + diss	X + diss	X + diss	-
Manganese - Mn	X	X	Х	X	X + diss	X + diss	X + diss	X + diss	-
Nicklel - Ni	Х	X	Х	X	X + diss	X + diss	X + diss	X + diss	-
Zinc - Zn	X	X	Х	X	X + diss	X + diss	X + diss	X + diss	-
Aluminum - Al	Х	X	Χ	X	X + diss	X + diss	X + diss	X + diss	-
Total Diss Sol - TDS	Х	X	Χ	X	X	X	Χ	X	-
Sodium - Na	-	X	-	X	Х	Х	-	X	X
Boron - B	-	X	-	X	Х	X	-	X	-
Selenium - Se	-	X	-	X	Х	Х	-	X	-
Barium - Ba	-	Х	-	X	Х	Х	-	X	-
Strontium - Sr	-	X	-	X	Х	X	-	X	-
Bromide - Br	-	X	-	X	Х	Х	-	X	-
Osmotic Pressure - OP	-	X	-	Х	Х	Х	-	Х	-
Total Org C - TOC	-	-	Х	X	-	-	-	-	-
Arsenic - As	-	-	-	-	Х	X	-	-	-
Cadmium - Cd	-	-	-	-	Х	Х	-	-	-
Bio Oxy Demand - BOD-5day	-	-	-	-	Х	-	Х	-	-
Acidity - Acidity	-	-	-	-	-	Х	Х	-	-
Diss Org C - DOC	-	-	-	-	-	-	-	-	Х
Potassium - K	-	-	-	-	-	-	-	-	X

Grab samples will be the method of collection for bacteria. Currently sampling equipment is not sterilized; therefore, bacteria samples should be collected as grab samples from the center of flow in accordance with the NFM, Chapter 7. To collect this sample, open and close the bottle under the water surface. If flow conditions do not permit a wading sample, a sterile 1-L glass amber bottle may be placed in the weighted bottle sampler to collect the bacteria sample.

Samples collected for TOC or DOC should not touch plastic; therefore, grab samples in a glass brown amber bottle are preferable to the vertical integration samplers. Under high flow conditions a 1-L brown amber bottle placed in the weighted bottle sampler can be used to collect the TOC/DOC sample. If a cleaned Teflon bottle and nozzle is available, that can be used to collect the TOC/DOC sample as well, however, this equipment may not be available to each sampling team.

Samples should not be collected on Fridays because the DEP lab does not process any samples on Saturdays. Bacteria samples should be collected on Mondays, Tuesdays, or Wednesdays and as late in the day as possible. The holding times and incubation time prevent samples collected on Thursdays and Fridays from being analyzed during normal business hours.

Sequence Numbers

Samples are identified by sequential numbers that are assigned to each sampler. Each sample should be assigned the next sequential number. This number is used to enter and track each sample collected from sampling through analytical results. If sequence numbers are skipped please notify the project chief and the DEP data manager. If sequence number 999 is reached the next number rolls over to 001.

Labeling of Bottles

Sample bottles that get submitted to the PADEP laboratory need to be labeled with the following information:

- WQN #
- Collector ID #
- Sequence #
- Date
- Time
- SAC Code
- Preservative (if any)
- Filtered (if performed)

Sample Preservation

Once the samples have been split into their respective bottles, they should then be preserved with the appropriate acid (nitric, sulfuric,), per Table 2. After sample preservation has been completed, the samples should be kept in a cooler with ice.

Equipment Cleaning

Cleaning procedures are detailed in NFM, Chapter 3.2.1 – Cleaning of Equipment Used to Sample for Inorganic Constituents. No significant deviations from the National Field Manual are noted except for the requirement to soak the Churn Splitter for in detergent solution for 30 minutes. Start the cleaning step as early as possible in the processing, do preservation, paperwork, and packing of samples in the interim, and allow the splitter to soak as close to 30 minutes as feasible given the time constraints of your daily sampling schedule.

If field-cleaning of equipment is necessary, it is recommended that four 5-gallon plastic containers be transported in the vehicle. One container of each of the following:

- Detergent water (0.1 percent v/v ratio of Liquinox: tap water)
- Tap water
- Acid rinse (5 percent v/v ratio of ACD trace-element grade hydrochloric acid: de-ionized water)
- De-Ionized Water

Field Forms

When obtaining a water sample, notes, observations and field measurements should be recorded on U.S. Geological Survey Surface Water-Quality field sheets (see Appendix A). It is helpful to copy these field sheets onto Rite-in-the-Rain paper.

Sample Transportation

At the end of each sampling day, water samples should either be dropped-off at the PADEP laboratory or PADEP's contracted courier drop-off/pick-up location with a bill of lading. PADEP's contracted courier service makes routine visits to their pre-determined site locations and delivers the samples to the PADEP laboratory by 8:00 a.m. the following day.

REFERENCES CITED

Department of Environmental Protection. 2012. <u>Pennsylvania's Surface Water Quality Monitoring Network (PSWQN).</u> 3800-BK-DEP0636 – revised 10/2012.

United States Geological Survey. National Field Manual for the Collection of Water-Quality Data (NFM).

APPENDIX A

U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY FIELD FORM



U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY NOTES

NWIS Record No.

QW Station No	QW Station Name						
WQN ID	Sample Date	Sample Time					
_		Cost Center Code:					
		rol) Q Station No Hydrologic Condition					
		c. QA Time Assoc. Seq. #					
		Additional Test:					
Start time GHT	Time GHT Time	GHT End Time GHT _					
	Field Measurem	nents					
Gage ht.(00065)	ft Q, inst (00061)	cfs Water Temp (00010)	0C				
Air Temp(00020)	0C pH (00400)	units sp.Cond(00095)	S/cm				
Dis. Oxygen (00300)	mg/L DO Sat (00301)	% Bar. Pres (00025)	_mm Hg				
Turbidity (63680)	FNU WW Check Bar	ft					
	Sampling Inforn	nation					
Sampler Type(84164)	Sampler ID	Sample Splitter Type(84171)					
Sample Bottle Material:	plastic teflon Nozzle Material:	plastic teflon Nozzle Size: 3/16 1/4	1 5/16				
Sampling Method(82398	3): EWI(10) EDI(20) single vertical	l(30) multiple verticals(40) # of Verticals(40)	cals				
Stream Width: ft	mi Sampling Points:						
Hydrologic Condition: N	Not determined; (4) Stable, low stage	e; (5) Falling stage; (6) Stable, high stag	e;				
(7) Peak stage; (8) Rising	stage; (9) Stable, normal stage						
Sampling Location: wad	ling cableway boat bridge upstream	downstream side of bridge ft mi ab	bl gage				
Sampling Site: pool riffle	e open channel Bottom: bedrock roc	ck cobble gravel sand silt other					
Stream color: brown gre	en blue gray clear other Stream	Mixing: well-mixed stratified poorly-r	nixed unknown				
Weather: clear partly clear	oudy cloudy Precipitation: none 1	ight medium heavy snow sleet rain i	mist				
Wind: calm light breeze	gusty windy Temperature: very co	old cool warm hot					
No. days since last signif	ficant rainfall						
Observations [Codes: 0=nor	ne; 1=mild; 2=moderate; 3=serious; 4=e	extreme] Floating garbage(01320)Floa	ating algae				
mats(01325)Floating debris(01345)Turbidity(01350) Oil-grease (01300) Detergent suds (01305) Atm.							
Odor (01330) Fish kill ((01340)						

				Oueli	tv Contro	l Informo	tion					
			NUMBE 6N H	RS		ontrol Information 4.5N H2SO4						
Conc. H2SO4 NaOH							1:1 HCl _					
Blank V	Vater Soi	urce: Of	fice DI N	WOL Blank	Water							
	Vater Lot											
					Do	sticido (O	0202)					
						sucide (9)	9202)					
VOC/P	esticide (9	99204) _										
Filter Lo	ot Number	rs										
capsule				po	ore size		b	rand				
				Q'	W Meter I	nformati	on					
Meter N	Make/Mo	del			Meter	# (S/N)			Prob	e #		
Meter (Calibratio	on Infor	mation: at	tached in	meter log l	oook						
					N	otes						
					<u> </u>	49 BT 4						
Station	ft from	Time	Gage ht	Depth	Cross Sec	scion Note	DO	DO sat	pН	Turbidity		
Station	left	Time	ft.	ft	0C	□S/cm	mg/L	%	units	FNU		
	bank (00009)		(00065)	(81903)	(00010)	(00095)	(00300)	(00301)	(00400)	(63680)		
	or right				(Method	(Method	(Method		(Method	(Method		
	bank				Code)	Code)	Code)		Code)	Code)		
1	(72103)											
2 3 4												
4												
5												
6												
7												
8												
8												
10												
11												
12												
Entered	into SIS I	hv		Date			Entered in	NWIS	late			