

CHESAPEAKE BAY WATER-QUALITY MONITORING PROGRAM

MARYLAND RIVER INPUT MONITORING (RIM) PROGRAM AND NONTIDAL NETWORK (NTN) STATIONS NUTRIENT AND SEDIMENT LOADING AND TRENDS COMPONENT

QUALITY-ASSURANCE PROJECT PLAN

JULY 1, 2017 to JUNE 30, 2018

MARYLAND DEPARTMENT OF NATURAL RESOURCES
Resource Assessment Service
Tidewater Ecosystem Assessment
Annapolis, Maryland

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Chesapeake Bay Program Office
Annapolis, Maryland

IN COOPERATION WITH THE
U.S. GEOLOGICAL SURVEY
Maryland-Delaware-D.C. Water Science Center
Baltimore, Maryland

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QUALITY-ASSURANCE PROJECT PLAN (QAPP)

for the

Maryland River Input Monitoring Program and Nontidal Network Stations

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A. Project Management

A.1 Introduction

This Quality-Assurance Project Plan (QAPP) describes quality-assurance goals and measures for the Maryland River Input Monitoring (RIM) Program and the Nontidal Network (NTN) designed to support Chesapeake Bay restoration programs.

The project, the *Chesapeake Bay River Input Monitoring Program*, includes the monitoring of nutrient and suspended-sediment concentrations and streamflow in selected Maryland rivers representing major inflow to Chesapeake Bay. This project is supported through Maryland's Department of Natural Resources (MD DNR) and U.S. Geological Survey (USGS) cooperative funds. The objectives of this project are to:

- Characterize nutrient and suspended-sediment concentrations in terms of flow and load for four (4) major tributaries to the Chesapeake Bay in Maryland at or above the head of tide, including the Susquehanna River at Conowingo, Maryland; the Potomac River at Chain Bridge, at Washington, D.C.; the Patuxent River near Bowie, Maryland; the Choptank River near Greensboro, Maryland;
- Determine trends that might develop in response to nutrient- and sediment-control programs in the Bay's major watersheds;
- Provide nutrient and suspended-sediment data for calibration of the Chesapeake Bay Watershed model (WSM) and loading inputs to the Chesapeake Bay Water-Quality (WQ) model; and
- Integrate the information collected in this program with other elements of the monitoring program to gain a better understanding of the processes affecting the water quality of the Chesapeake Bay.

The MD DNR and the USGS conduct this project cooperatively. Sampling events, goals, and objectives for this project are overseen by the USGS Project Chief, Joel Blomquist, and the USGS Project Field Manager, Brenda F. Majedi.

The project, the *Chesapeake Bay Nontidal Network*, includes the monitoring of nutrient and suspended-sediment concentrations and streamflow of about 120 water-quality monitoring stations operated across the watershed; four stations (listed below) representing the small and/or urban watershed component are monitored by USGS MD-DE-DC personnel. All water-quality sample collection is consistent with protocols set forth by the Chesapeake Bay Program partnership. This network provides the principal data for reporting of water-quality conditions in the watershed, including nutrient and sediment loads and trends in loads and concentrations. The primary objectives of the Chesapeake Bay Nontidal Watershed Water-Quality Network are to:

- Quantify sediment and nutrient loads in the tributary strategy basins of the Chesapeake Bay watershed;
- Assess the factors affecting nutrient and sediment status and trends;
- Improve calibration and verification of partners' watershed models;
- Estimate changes over time (trends) in sediment and nutrient concentrations that are related to the implementation of Best Management Practices, or other anthropogenic factors.

The USGS is one of several participating partner agencies, and provides nutrient and suspended-sediment concentration data for the following four monitoring stations in the network, which were chosen to represent the small and/or urban watershed component:

- Chesterville Branch near Crumpton, MD
- Watts Branch at Washington, D.C.
- Rock Creek near Joyce Road, Washington, D.C.
- Hickey Run at National Arboretum at Washington, D.C.

The results from this monitoring program will eventually fold into results for the entire Chesapeake Bay NTN, which requires five years of data following NTN protocols to estimate loads and at least 10 years of data to estimate trends (Langland and others, 2012).

A.2 Distribution List

This QAPP will be distributed to the following project participants:

Joel Blomquist, USGS MD-DE-DC Water Science Center, Project Chief, 443-498-5560
Brenda Majedi, USGS MD-DE-DC Water Science Center, Project Field Manager, 443-498-5527
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A.3 Project/Task Organization

Joel Blomquist, USGS, is the Project Chief for the Maryland River Input Monitoring Program and the USGS Maryland Nontidal Network. He is responsible for the technical design, operation, and execution of the respective programs as outlined in the annual scope of work to MD DNR. Also, he is responsible for evaluating and describing the data collected for the program, meeting the quality-assurance and quality-control goals for the program, and producing USGS reports.

Tom Parham is MD DNR's Chesapeake Bay Program Grants Coordinator. He is responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other administrators, and coordination with cooperating agencies and institutions, and approves the technical design, conduct, and data analysis of the program. He also is tasked with assuring that all project commitments, the project timetable, and deliverables are completed.

Charles Walker is the USGS MD-DE-DC Water Science Center (WSC) Water-Quality Specialist. As a quality-assurance officer, he is tasked with conducting field audits and reviewing reports. While these are regular responsibilities of the USGS WSC Water-Quality Specialist, he may recommend additional quality-control activities to the USGS Project Chief if necessary. His responsibilities are generally limited to activities in the MD-DE-DC WSC, and he may request assistance from water-quality specialists in the Virginia and Pennsylvania WSC for activities in those offices.

A.4 Problem Definition/Background

The decline in water quality of the Chesapeake Bay within the few last decades has, in large part, been attributed to excessive nutrients entering the estuary from its surrounding tributaries. In an effort to improve the water quality of the Bay, Federal, State, and local governments have initiated point and non-point source nutrient-reduction programs within the tributary basins discharging to the Bay. Monitoring at key sites can help to quantify improvements in water quality and verify the effectiveness of nutrient-control measures implemented in the watersheds.

In addition, the quality of the river discharge, and the timing and magnitude of the pollutant concentrations and loads delivered to the estuary are important data needed to enhance knowledge of or need to strengthen other components of the Chesapeake Bay water-quality monitoring program. The integration of all of these components leads to a better understanding of the factors influencing water quality that can then be translated into better water-quality management for the Bay and its tributaries.

With these general goals in mind, the Maryland Department of Natural Resources' (MD DNR) Resource Assessment Service, in cooperation with the USGS, initiated the Maryland River Input Monitoring (RIM) component of the Chesapeake Bay Water-Quality Monitoring Program. Four major tributaries to the Chesapeake Bay – the Susquehanna, Potomac, Patuxent, and Choptank Rivers – were initially selected for the River Input Monitoring Program in 1985 by the State of Maryland. Combined, these rivers contribute over 70 percent of the flow to the entire Chesapeake Bay and they contribute nutrients and suspended sediments from a wide range of

land-use, geologic, and hydrologic conditions found in the Bay watershed. Monitoring stations were established near the most downstream non-tidally affected portion of each above-named river to monitor nutrient and suspended-sediment concentrations and streamflow. Data collected from these four monitoring stations are used to calculate nutrient and suspended-sediment loadings and transport to tidal tributaries of the Bay.

In addition to the RIM program, the USGS coordinates and collects water-quality data at the following stations as part of the Chesapeake Bay Program Nontidal Network (NTN) for long-term monitoring of agricultural or urban watershed inputs into the Chesapeake Bay: Chesterville Branch near Crumpton, Maryland, and Watts Branch, Hickey Run, and Rock Creek, in the District of Columbia. In Water Year 2011, the Chesterville Branch station was added to the network to represent the agricultural land-use component. In Water Year 2013, Watts Branch, Hickey Run, and Rock Creek were added to the network to represent the small, urban land-use component. A consortium of members from the Environmental Protection Agency, the Chesapeake Bay Program, the Washington, D.C. District Department of the Environment, and the U.S. Geological Survey chose the three urban stations that best represent urban land use and basin size and on the ability to instrument and collect representative suspended-sediment and nutrient data suitable for long-term analysis of loads and trends in accordance with existing NTN methods. Inclusion of above-named streams adds under-represented sites to a network historically oriented towards larger watersheds.

A.5 Project/Task Description

At each monitoring station, water-quality samples representative of the entire river cross section are collected using USGS protocols to determine concentrations of selected nutrient species and suspended sediment in the river. Samples for water-quality analysis are collected on a monthly, fixed-frequency basis at each monitoring station as well as during stormflow events. Samples are collected during all four seasons and across different flow regimes in order to capture seasonal and hydrologic variability of the water quality at each station. When combined with the continuous, 15-minute flow record from the USGS stream gage at each station, it is possible to estimate nutrient and suspended-sediment loads on a monthly and annual basis with a known level of confidence. Additionally, water-quality field measurements are made for dissolved oxygen, pH, specific conductance, water temperature, and air temperature.

The USGS's National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated, accessed here: <http://water.usgs.gov/owq/FieldManual/>) describes the USGS sample-collection protocols in detail. Data-collection quality will be monitored by the assessment of field blanks and replicates and by annually conducting and documenting the results of random field audits. Additional documentation is listed in the MD-DE-DC WSC internal quality-assurance plan. In addition, the guidance is followed as set forth in the U.S. Environmental Protection Agency (USEPA) Chesapeake Bay Program (CBP) Methods and Quality Assurance for CBP Water Quality Monitoring Programs, Chapter 5, Nontidal Water Quality Monitoring, accessed here: http://www.chesapeakebay.net/channel_files/19225/chapter_5-ntn_3-30-16.pdf.

Samples for water-quality analysis are collected on a monthly, fixed-frequency basis, as well as during stormflow events. An electronic project field data sheet is completed for each sample using USGS PCFF (personal computer field form) software ; an example of data recorded for each water-quality sample collected is listed in Attachment A. Data are electronically uploaded to the USGS National Water Information System (NWIS) data management system using the PCFF software. Water-quality data are reviewed when received from the laboratory. Final streamflow data for the four River Input Monitoring stations will be forwarded to the Project Coordinator at MD DNR by April 15 following the previous water year, and updated monthly and annual loads by July 15. USGS nutrient, chlorophyll (analyzed by MD DHMH laboratory), and suspended-sediment data will be uploaded directly to the EPA Chesapeake Bay Program (CBP) via DUET.

Quarterly progress reports describing field and other project activities and issues will also be submitted to the Project Coordinator. Additionally, data interpretation of RIM nutrient trends and trend explanation will be performed by project hydrologists and incorporated into various USGS and/or MD DNR reports.

A.6 Data-Quality Objectives and Criteria for Measurement Data

The data collected for the RIM program and the Chesapeake Bay Nontidal Network program provides Chesapeake Bay resource managers with information that can help to quantify changes in water quality, quantify nutrient loads critical for evaluating progress towards reducing controllable nutrients to the Bay, and verify the effectiveness of nutrient-control measures taken in the watersheds. A calibrated model was developed that can simulate constituent relationships, seasonal variation, and changes in trends. As a result, water-quality samples need to be collected monthly throughout the year under different streamflow conditions to determine loads within a known confidence interval. Once completed, this information is then given to researchers and Bay resource managers.

Several laboratories provide data for the four Maryland RIM stations and the Nontidal Network stations. The USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, provides the nutrient analyses; the USGS Kentucky Sediment Laboratory, in Louisville, Kentucky, provides the suspended-sediment analyses; and the Maryland Department of Health and Mental Hygiene (MD DHMH) Laboratory in Baltimore, Maryland, provides the chlorophyll-A analysis for the RIM program stations. Detailed quality-assurance procedures are described for each laboratory at the following links: the NWQL in Mahoney (2005), available at <http://pubs.usgs.gov/of/2005/1263/pdf/OFR2005-1263.pdf>; the USGS Kentucky Sediment Laboratory in Shreve and Downs (2005), available at <http://pubs.usgs.gov/of/2005/1230/>; and the MD DHMH available at <http://dhmh.maryland.gov/laboratories/docs/enviroguide.pdf>

A.7 Special Training

Field personnel are trained in USGS water-quality sample-collection protocols, record management, quality-assurance procedures, vehicle operations, and water-quality instrument maintenance and troubleshooting. Laboratory personnel must be trained in analytical methods, quality-control procedures, record management, and instrument maintenance and troubleshooting.

A.8 Documentation and Records

Water-quality field measurements of water and air temperature, dissolved oxygen, pH, and specific conductance are recorded on the project field sheet for each sample collected. All data are recorded using standardized field data sheets (Attachment A). These data are electronically entered into the USGS NWIS data management system by the technicians who collect the data. These data are provided electronically to MD DNR.

Water-quality samples for the RIM and NTN programs are submitted for nutrient analysis to the USGS NWQL in Denver, Colorado. A customized laboratory schedule is requested for each sample submitted: NWQL Schedule 1965 is requested for the four RIM program stations; Schedule 2580 is requested for the Watts Branch, Hickey Run, and Rock Creek stations (Attachments B₁ and B₂); and Schedule 2755 with adds of particulate N, dissolved phosphorus, and total phosphorus is requested for the Chesterville Branch station. Suspended sediment is collected for each sample collected and is analyzed at the USGS Sediment Laboratory in Louisville, Kentucky; and chlorophyll-A is collected with the RIM station samples is analyzed at the Maryland Department of Health and Mental Hygiene (MD DHMH) Laboratory in Baltimore, Maryland. Each laboratory has its own specific analytical services request form (ASR), which is completed and mailed with each sample. Attachment C is an example of the ASR sent to the NWQL for the Maryland RIM program.

All paper and electronic records, including calibration information, are archived at the USGS MD-DE-DC WSC per USGS protocol.

A web site has been created to provide detailed information about the RIM project as well as simple access to Maryland's concentration and load data. The site includes general information, data retrieval options, a water

chemistry page that describes sources and chemical behavior of the water-quality constituents, trends in the constituents, methods used in the project, Chesapeake Bay related publications and links, a glossary, and a bibliography. This site can be accessed at: <http://va.water.usgs.gov/chesbay/RIMP/>

B. Measurement/Data Acquisition

B.1 Experimental Design

This document provides a detailed description of the monitoring and analysis components of a study conducted by the MD DNR Assessment Service and the Chesapeake Bay Program Nontidal Network, in cooperation with the USGS, to quantify nutrient and suspended-sediment loads entering the Chesapeake Bay to determine trends in constituent-concentration data occurring at these tributary stations.

The number of events to be sampled and the number of samples per event are based on the requirements of the load-computation model. Water-quality samples are collected on a monthly, fixed-frequency basis and during varying stormflow conditions (about 8 to 10 stormflow samples per site per year) in order to capture the hydrologic and seasonal variability of nutrient and suspended-sediment concentrations. Continuous 15-minute flow measurements are also collected. Using a multivariate model, the seasonal relationship between constituent concentration and streamflow at each site is established. Using the continuous flow record, a cumulative load of nutrients and suspended sediment can be determined.

Station Description

The location of the four Maryland RIM water-quality monitoring stations was chosen by determining the location of existing stream-gaging stations near the most downstream nontidal reach of each selected river. The monitoring stations selected for the Maryland RIM program are located on the Susquehanna River at Conowingo, Maryland; the Patuxent River near Bowie, Maryland; the Choptank River near Greensboro, Maryland; and the Potomac River at Chain Bridge at Washington, D.C. The NTN monitoring stations were selected to represent varying land use and basin size, and are located at Chesterville Branch near Crumpton, MD; Watts Branch at Washington, D.C.; Rock Creek at Joyce Road, Washington, D.C.; and Hickey Run at National Arboretum at Washington, D.C. The location of the monitoring sites and drainage area information are presented in Table 1.

Table 1. Location of the Maryland River Input Monitoring Program and Nontidal Network water-quality stations (listed in descending order of drainage area)

Station Name	USGS Station	Latitude deg-min-sec	Longitude deg-min-sec	Drainage (sq. mi.)
Susquehanna River at Conowingo Dam, MD	01578310	39-39-28	76-10-29	27,100
Potomac at Chain Bridge River, D.C.	01646580	38-55-46	77-07-02	11,570
Patuxent River nr. Bowie, MD	01594440	38-57-21	76-41-36	348
Choptank River nr. Greensboro, MD	01491000	38-59-50	75-47-10	113
Rock Creek at Joyce Road, Washington, D.C.	01648010	38-57-37	77-02-31	63.7
Chesterville Branch nr Crumpton, MD	01493112	39-15-25	75-56-24	6.1
Watts Branch at Washington, D.C.	01651800	38-54-04	76-56-32	3.28
Hickey Run at National Arboretum at Washington, D.C.	01651770	38-55-00	76-58-09	0.99

B.2 Sampling Method

USGS personnel collect water-quality samples at each site in accordance with Chapter A4 of the USGS National Field Manual for the Collection of Water Quality Data (U.S. Geological Survey, variously dated).

Water-quality samples are collected on a monthly, fixed-frequency basis and during varying high-flow (stormflow) conditions on a seasonal basis, in order to capture the hydrologic and seasonal variability of nutrient and suspended-sediment concentrations. Twelve monthly, fixed-frequency samples and about 8 to 12 stormflow samples are collected at each site per year. The average stormflow coverage is two to three samples per season per site; stormflow sample collection depends largely upon hydrologic and meteorologic conditions, as well as safety considerations. The monitoring program emphasizes the collection of water-quality samples during periods of stormflow because most of the river-borne nutrient and suspended-sediment load is associated with storm events. Discrete samples are collected during selected storm events over the rise, peak, and falling limb of the hydrograph. Water-discharge data are also collected for each of the rivers throughout the period.

A stormflow (or high-flow) event is defined as a significant increase in discharge based on the antecedent precipitation, the magnitude of discharge, and the season of the year. Storms selected for sampling are dependent on flow conditions and the previous sampling history. An attempt is made to sample a representative range of storm types and sizes throughout the year. Operational definitions of stormflow conditions are described for each of the monitoring sites and are used as guides for sample-collection procedures. These, however, are not meant to be rigid definitions of stormflow conditions. Stormflow events are predicted through weather forecasts, precipitation amounts, and river stage.

Water-quality samples are collected at each of the sites listed below using isokinetic, depth-integrated sampling techniques when flow conditions warrant, which provide samples representative of stream conditions. A DH-81 (hand-held), DH-95 (weighs 35 pounds), or D-95 (weighs 65 pounds) isokinetic sampler, or a stainless-steel

weighted-bottle sampler, is used depending upon river flow conditions -- at least 1.5 cubic feet per second of flow is required to collect a sample using the isokinetic sampler. The DH-81, DH-95, and D-95 isokinetic samplers are composed of a white-painted aluminum body with Teflon fins, and use a Teflon nozzle; they are fitted with a one-liter sample-collection bottle made of Teflon or polyethylene. Sampler selection is site dependent.

The weighted-bottle sampler, used when river discharge conditions do not warrant isokinetic sampling, or where unique logistical and safety issues preclude the use of isokinetic sampling devices, is made of stainless steel and holds a one-liter bottle made of Teflon, polyethylene, or glass. The weighted-bottle sampler is lowered to the water with a hand reel and synthetic rope (nylon or polyethylene) configuration. There is about an eight-inch unsampled zone due to the distance from the channel bottom to the sample bottle neck's opening.

The general approach for the collection of water samples is the Equal-Width Increment (EWI) sampling method in which an equal transit-rate technique is used while lowering the sampler. This method involves the collection of water-quality samples at the centroids of equal-width increments along the river cross section. Samples are collected at eight to ten sections of the river, yielding a cross-sectional, depth-integrated sample; minor variations in the technique are used to conform to site conditions. Samples are collected along the width of the stream and composited into a churn splitter, which is a device that homogenizes the water-sediment mixture. Subsamples for laboratory analysis are filled from the churn splitter. All sample-collection and processing equipment is prewashed following stringent protocols to minimize contamination.

Beginning Water Year 2013, samples for suspended-sediment analysis are collected directly from the river when isokinetic samplers are used to collect the water-quality sample in order to be consistent with the USGS National Stream Quality Accounting Network (NASQAN) and National Water Quality Assessment (NAWQA) national programs. Samples are sent directly to the USGS Kentucky sediment laboratory for analysis of concentration; percent sand-fines is typically requested for storm samples. Samples are either composited at the laboratory, or analyzed separately for QC purposes. Previously, suspended-sediment samples were collected from either the churn splitter or directly from the stream depending on flow conditions and QC requirements. This information is noted on the field form.

Susquehanna River

USGS personnel collect water samples from the Susquehanna River at the Conowingo Dam in Conowingo, Maryland (USGS Site ID 01578310). Samples are collected using the equal-discharge-increment method with the stainless-steel weighted-bottle sampler fitted with a one-liter (two-inch mouth) Teflon sampler bottle suspended by a polyethylene rope. Isokinetic samplers such as the D-95 are not an appropriate method for sampling this site due to the churning action of the water from the turbine outflows.

Restricted access on the Susquehanna River at Conowingo Dam requires that a variation of Equal-Discharge Increment (EDI) sampling be used. This method involves the collection of water-quality samples at the centroids of equal discharge increments along the turbine outflow. The sampler is suspended from the catwalks at the turbine outflow. The number and location of cross-section samples are dependent on the characterization of flow from the turbines at the time of sampling. Previous testing at Conowingo Dam has shown that this approach provides a representative sample for flows confined to the turbines. However, sampling from the turbines can be unrepresentative of spillway discharges since the flows originate from different locations in the reservoir's vertical profile. Sampling from the spillway during stormflow events is not allowed due to safety and security concerns. Storms on the Susquehanna are operationally defined as occurring when water passes over the spillway. This represents a storm discharge exceeding 80,000 cubic feet per second (ft^3/s), the maximum turbine capacity.

The USGS NASQAN (National Stream Quality Accounting Network) program was restarted in January 2008 at the Susquehanna River site. In addition to the routine RIM constituents, pesticides and major ions are collected. Two minor changes to sample-collection and processing protocol are necessary to accommodate the NASQAN

program: (1) a two-person sampling team collects the samples; and (2) samples are composited into a Teflon churn splitter. NASQAN is a fixed-frequency sampling program. Fourteen samples are collected in each water year; some months have semi-monthly sample collection.

In mid-water year 2010, the NASQAN program has added support for analysis of bacterial DNA at the Susquehanna River site. Dr. Byron Crump, formerly of the University of Maryland Center for Environmental Science Horn Point Laboratory, analyzes the samples. This collaboration will help to describe the genetic diversity of bacterioplankton in large rivers of the United States. The sampling protocol has been tested and refined at two large river systems in the NASQAN network.

Potomac River

USGS personnel collect water samples from the Potomac River at Chain Bridge in Washington, D.C. (USGS Site ID 01646580) using the EWI method. Water-quality samples are collected using a stainless-steel weighted-bottle sampler fitted with a one-liter (two-inch mouth) Teflon bottle. The number and location of cross-section samples are dependent on the characterization of flow at the time of sampling. During most flow conditions, samples are collected from five points along the river cross section from Chain Bridge. Depth-integrated, isokinetic samplers cannot be collected at Chain Bridge because flow conditions exceed the limits of the samplers. Previous testing has shown that the water column at this location is well-mixed and samples within the near-surface zone (1-2 meters) are considered to be representative of the stream's vertical profile.

During stormflow conditions, samples are collected with the stainless-steel weighted-bottle sampler fitted with a one-liter Teflon bottle suspended by a polyethylene rope from five points along the river cross section from Chain Bridge. Isokinetic samplers such as the D-95 are not an appropriate method of sampling off Chain Bridge due to lack of a sampling platform as a result of high volumes of traffic on Chain Bridge. Samples are composited into a Teflon churn splitter. A storm event on the Potomac River at Chain Bridge is operationally defined as a USGS gage height at Little Falls Dam of greater than 5 feet or a discharge of greater than 20,000 cubic feet per second (cfs or ft³/s). There is occasion when stormflow samples are collected below these thresholds, typically after a runoff event following a dry spell.

The NASQAN program was also integrated into the sample collection activities at the Potomac River at Chain Bridge site beginning January 2008. This program will piggyback on the USGS National Water Quality Assessment (NAWQA) program already in place. In addition to the routine NAWQA parameters, major ions will be collected each month. Eighteen NASQAN samples are collected in each water year.

In mid-water year 2010, the NASQAN program has added support for analysis of bacterial DNA at the Potomac River site. Dr. Byron Crump of the University of Maryland Center for Environmental Science Horn Point Laboratory will analyze the samples. (<http://hpl.umces.edu/faculty/bcrump/resar.htm>). This collaboration will help to describe the genetic diversity of bacterioplankton in large rivers of the United States. The sampling protocol has been tested and refined at two large river systems in the NASQAN network.

In May 2010, additional modifications were made to the analytical list used in the coordinated RIM/NAWQA/NASQAN sampling at Potomac River. Because the NAWQA/NASQAN analytical suites do not encompass all of the desired constituents for RIM, we decided to increase the NWQL schedule requests for each routine NAWQA/NASQAN scheduled sample to include all RIM parameters.

During the period August 2009 through January 2011, Chain Bridge was under construction, which severely limited access to the river from the bridge. This necessitated a modification to sample-collection protocol at Chain Bridge -- samples were collected from the automatic sampler maintained by the OWML (Occoquan Water Monitoring Laboratory), and in a few cases from a weighted bottle near the automatic sampler intake. A quality-assurance sampling plan was developed by the NAWQA and NASQAN programs to test for potential bias in results for these sampling modifications during this period. Replicate samples were collected during 2011 to

evaluate the comparability of samples collected as a composite along the normal cross section (bridge) and those collected from the pump. In general, single replicates were collected for dissolved analytes and triplicates were collected for suspended analytes over low-, medium-, and high-flow conditions. Results show that pump-collected and cross-section-collected data are generally comparable.

Patuxent River

USGS personnel collect water samples at the Patuxent River at Governors Bridge on Governors Bridge Road in Bowie, Maryland (USGS Site ID 01594440). Cross-sectional, depth-integrated water-quality samples are collected manually at 8 to 10 sections along the bridge. Samples are collected using a stainless-steel weighted-bottle sampler fitted with a one-liter (one-inch mouth) Teflon bottle suspended by a polyethylene rope. Samples are composited into a polyethylene churn splitter.

During stormflow conditions, samples are collected using a DH-95 or D-95 isokinetic sampler. A storm event on the Patuxent River at Bowie is operationally defined as a USGS gage height of greater than about 7 feet or a discharge of greater than 800 cubic feet per second (cfs or ft³/s). There is occasion when stormflow samples are collected below these thresholds, typically after a runoff event following a dry spell.

Choptank River

USGS personnel collect water samples at the Choptank River nr Greensboro, MD (USGS Site ID 01491000) at located at the end of Red Bridges Road in Christian Park. Prior to the spring of 2000, an abandoned automobile bridge across the river served as the sampling platform. For safety reasons, the bridge was removed by the Caroline County Department of Public Works. The bridge was replaced as a sampling platform in fall 2001 by a cableway system constructed by the USGS. The cableway with A-frame anchors is a standard USGS river crossing system that is often used to sample inaccessible rivers.

Samples at the Choptank River are collected by wading in the river when flows allow, using the DH-81 isokinetic sampler fitted with a one-liter Teflon bottle. Samples are collected at 8 to 10 points along the river cross section. During extreme low-flow conditions, samples are collected at the gage control (v-notch weir) with a one-liter Teflon bottle filled manually.

During stormflow events, sampling is performed with a DH-95 or a D-95 isokinetic sampler operated from a remote-controlled Hornet sampler along the cableway that traverses the river. (In May 2010, the cableway was modified to use this remotely-control sampler that is operated from the stream bank. This was done in order to improve safety for sampling staff. During high-flow conditions, samples continue to be collected using EWI methods and isokinetic samplers.) There is occasion when stormflow samples are collected below these thresholds, typically after a runoff event following a dry spell.

Occasionally, storm samples will be collected about 100 feet downstream of the cableway when stream conditions are wadeable (gage height of about ≤ 3.50 feet). A storm event on the Choptank River near Greensboro is operationally defined as a USGS gage height of greater than 4 feet or a discharge of greater than 400 cubic feet per second (cfs or ft³/s). There is occasion when stormflow samples are collected below these thresholds, typically after a runoff event following a dry spell, where a discharge of at least twice that of the pre-storm discharge is deemed appropriate for sample collection.

Chesterville Branch

USGS personnel collect water samples at the Chesterville Branch nr Crumpton, MD (USGS Site ID 01493112) located off of River Road (Rte. 291), about 90 feet upstream from the surface-water gage located at River Road. Prior to July 2011 water-quality samples were collected at the gage located at the downstream side of the culvert of River Road, but several major storms events severely altered the stream cross section, precluding water-quality sample collection at the gage. Samples are collected monthly on a fixed-frequency basis, and during storm events.

Samples at the Chesterville Branch site are collected using EWI techniques from 8-10 locations along the river cross section using the DH-81 isokinetic sampler fitted with a one-liter Teflon bottle. Samples are collected by wading in the river when flows allow; during extreme low-flow conditions, grab samples are also collected at 8-10 locations. During high-flow events when conditions preclude wading, samples are collected from the downstream side of the bridge using a DH-95 isokinetic sampler.

Watts Branch

USGS personnel collect water samples from Watts Branch at Washington, D.C. (USGS ID 01651800) 10 feet upstream from the Minnesota Avenue Northeast bridge in Washington, D.C. EWI fixed-frequency samples are collected using a DH-81 isokinetic sampler equipped with an appropriate nozzle dictated by stream depth and velocity at time of sampling. When EWI conditions are not present, a DH-81 without a nozzle is used to collect an equal width, nonisokinetic sample. Samples are composited into an 8-liter polyethylene churn splitter, processed, and shipped overnight to the National Water Quality Laboratory in Denver, CO for analysis. Additionally, suspended-sediment samples are collected from each in-stream sampling location and sent to the USGS sediment lab in Louisville, KY for composite concentration and sand/fine analysis. Very-high stormflow conditions require samples to be collected using a DH-95 or D-95 isokinetic sampler.

The sewershed nature, engineering, and morphology of Watts Branch make defining a storm event difficult. The operational definition of a storm event is a stage twice that of base flow with no associated precipitation, i.e. flow induced by point source pollution (broken sewer or water main) or an increase in stage associated with a rainfall rate ≥ 0.4 inches per hour.

Hickey Run

USGS personnel collect water samples from Hickey Run at National Arboretum in Washington, D.C (USGS ID 01651770). Equal width, depth-integrated, isokinetic water-quality (EWI) samples are collected from a cross-section approximately 100 yards south of New York Avenue where the stream emerges from a subterranean, engineered channel. Fixed-frequency samples are collected using a DH-81 equipped with an appropriate nozzle dictated by stream depth and velocity at time of sampling. When EWI conditions are not present, a DH-81 with no nozzle is used to collect an equal width, nonisokinetic sample. Samples are composited in an 8-Liter, polyethylene churn sample splitter, processed, and shipped overnight to the National Water Quality Laboratory in Denver, CO for analysis. Additionally, suspended-sediment samples are collected from each in-stream sampling location and sent to the USGS sediment lab in Louisville, KY for composite, sand/fine analysis. Very-high stormflow conditions require samples to be collected using a DH-95 or D-95 isokinetic sampler.

The sewershed nature, engineering, and morphology of Hickey Run make defining a storm event difficult. The operational definition of a storm event is a stage twice that of base flow with no associated precipitation, i.e. flow induced by point source pollution (broken sewer or water main) or an increase in stage associated with a rainfall rate ≥ 0.4 inches per hour.

Rock Creek

USGS personnel collect water samples from Rock Creek at the Joyce Road Bridge in Rock Creek Park near Washington, D.C (USGS ID 01648010). EWI fixed-frequency samples are collected using a water-quality configured DH-81 equipped with an appropriate nozzle dictated by stream depth and velocity at time of sampling. Some fixed frequency sample collection requires the use of a DH-95 due to elevated stream stage or velocity; typically in the winter/spring. When EWI conditions are not present, a water-quality configured DH-81 with no nozzle is used to collect an equal width, nonisokinetic sample. Samples are composited in an 8-Liter, polyethylene, churn sample splitter, processed, and shipped overnight to the National Water Quality Laboratory in Denver, CO for analysis. Additionally, suspended-sediment samples are collected from each in-stream sampling location and sent to the USGS sediment lab in Louisville, KY for compositing and analysis for concentration and percent sand/fines. If EWI conditions are not present at the time of sampling then suspended-sediment samples may be collected from the churn splitter.

During stormflow conditions, samples are collected using a DH-95 or D-95 isokinetic sampler. A storm event for Rock Creek at Joyce Road is operationally defined as a USGS gage height of greater than 2.5 feet or a discharge of greater than 160 cubic feet per second (cfs or ft³/s). On occasion, stormflow samples are collected below these thresholds; for example, after a runoff event following a dry spell.

Parameters Monitored

The parameters monitored as well as lab codes and analytical methods for the Maryland River Input Monitoring Program and the Non-tidal Network are shown in Table 2. Samples are analyzed at the USGS National Water Quality Laboratory (NWQL). Parameters analyzed are specific to each program: NWQL Schedule 1965 is requested for the four RIM program stations; Schedule 2580 is requested for the Watts Branch, Hickey Run, and Rock Creek stations (Attachments B₁ and B₂); and Schedule 2755 with adds of particulate N, dissolved phosphorus, and total phosphorus is requested for the Chesterville Branch station. Suspended sediment is analyzed for both programs at the USGS Sediment Laboratory in Louisville, Kentucky; and chlorophyll-A, monitored for the RIM stations only, is analyzed at the Maryland Department of Health and Mental Hygiene (MD DHMH) Laboratory in Baltimore, Maryland.

Field measurements, including water temperature, specific conductance, pH, dissolved oxygen, and turbidity will be measured at the same time samples are collected for chemical analysis, using methods described in the USGS National Field Manual.

Table 2. Maryland River Input Monitoring Program and Non-tidal Network parameters monitored

[Parm = parameter; LC – labcode; NWQL = USGS National Water Quality Laboratory; DHMH = Maryland Department of Health and Mental Hygiene Laboratory; mg/L = milligrams per liter; NFM = National Field Manual]

Lab Code	Parameter Code	Parameter/ Methodology	Reference	Reporting Level
Particulate Nitrogen (TPN)				
LC 2607 USGS	P49570	<i>Elemental Analysis on glass-fiber filter</i> EPA method 440.0	USEPA (1997)	0.017 mg/L
Total Dissolved Nitrogen (TDN)				
LC 2754 USGS	P62854	<i>Alkaline Persulfate digestion</i> I-2650-03	Patton and others (2003)	0.05 mg/L
Total Nitrogen (TN)				
	P00600	Total Nitrogen, calculated = P49570+P62854		
Dissolved Ammonia (NH₃)				
LC 3116 USGS	P00608	<i>Colorimetry, DA, salicylate-hypochlorite</i> I-2522-90	Fishman (1993)	0.01mg/L
Dissolved Nitrite as Nitrogen (NO₂)				
LC 1977 USGS	P00613	<i>Colorimetry, ASF</i> I-2542-89	Fishman (1993)	0.001 mg/L
LC 3156 USGS	PP0631	Dissolved Nitrite & Nitrate as NO₂+NO₃ <i>Colorimetry, DA, enzyme-reduction diazotization</i> I-2547-11	Patton and others (2011)	0.04 mg/L
LC 3157 USGS	PP0631	Dissolved Nitrite & Nitrate as NO₂+NO₃, NTN <i>Colorimetry, DA, enzyme-reduction diazotization</i> I-2548-11	Patton and others (2011)	0.01 or 0.04 mg/L
Total Phosphorus (TP)				
LC 2333 USGS	P00665	<i>Colorimetry</i> EPA method 365.1	Fishman and Friedman (1989)	0.004 mg/L
Total Dissolved Phosphorus (TDP)				
LC 2331 USGS	P00666	<i>Acid persulfate (filtered)</i> EPA method 365.1	Am. Public Health Assoc. (1995)	0.003 mg/L
LC 1978 USGS	P00671	Dissolved Orthophosphate (PO₄) <i>Colorimetry, ASF, phosphomolybdate</i> I-2606-89	Fishman (1993)	0.004 mg/L
LC 2612 USGS	P00681	Dissolved Organic Carbon (DOC) UV promoted persulfate oxidation, IR detection O-1120-92	Brenton and Arnett (1993)	0.23 mg/L
LC 2606 USGS	P00694	Total Particulate Carbon (TPC) EPA method 440.0	USEPA (1997)	0.05 mg/L
LC 2608 USGS	P00688	Particulate Inorganic Carbon (PIC) EPA method 440.0	USEPA (1997)	0.03 mg/L

LC 2611 USGS	P00689	Particulate Organic Carbon (POC) EPA method 440.0	USEPA (1997)	0.05 mg/L
LC 169 USGS	P00530	Total Suspended Solids (TSS) Residue at 105 deg C, gravimetric I-3765-89	Fishman and Friedman (1989)	15 mg/L
n/a	P80154	Total Suspended Sediment (SSC) <i>Filtration, evaporation</i> ASTM test method D3977-97 Method C	Shreve and Downs (2005) USGS Kentucky Sediment Lab	0.5 mg/L
LC 56 USGS	P00955	Dissolved Silica as SiO₂ <i>Colorimetry, ASF, molybdate blue</i> I-2700-89	Fishman and Friedman (1989)	0.06 mg/L
n/a DHMH	P32210	Chlorophyll A (Chlo-a) <i>Hydroscopic glass-fiber filtration</i>	MD DHMH Laboratory	0.1 mg/L
n/a	P00010	Water Temperature (°Celsius)	Field parameter, USGS NFM (variously dated)	0.1 mg/L
n/a	P00095	Specific Conductance (µS/cm)	Field parameter, USGS NFM (variously dated)	1 us/cm
n/a	P00400	pH (standard units)	Field parameter, USGS NFM (variously dated)	0.1 mg/L
n/a	P63680	Turbidity, FNU	Field parameter, USGS NFM (variously dated)	0.1 FNU
n/a	P00300	Dissolved Oxygen (mg/L)	Field parameter, USGS NFM (variously dated)	0.5 mg/L

B.3 Sample Handling and Custody

Sample Treatment and Preservation

Processing of water-quality samples collected by the USGS follow strict protocols which are documented in the USGS National Field Manual (U.S. Geological Survey, variously dated). Nutrient samples are composited in a pre-cleaned Teflon or polyethylene churn splitter. Samples for whole-water analysis are collected directly from the churn while churning at a rate of 1.0 ft/second. The whole-water samples are fixed with concentrated sulfuric acid (1 mL/125 mL of sample). Samples for dissolved-phase nutrients are collected with a peristaltic pump from the splitting device and filtered in line with a 0.45- μm (average pore size) polycarbonate capsule filter. All nutrient samples are placed immediately on ice and chilled to a temperature of 4 degrees Celsius. Samples are shipped on ice overnight to the NWQL in Denver, Colorado, according to USGS technical memorandum 02.04 (W.D. Lanier, 2002). This document can be found at (http://nwql.usgs.gov/Public/tech_memos/nwql.02-04.html).

Suspended-sediment samples, collected concurrently from the river with the water-quality samples, are shipped to the USGS Sediment Laboratory in Louisville, Kentucky, for analysis. Chain-of-custody procedures and protocols for analysis are documented in the quality assurance plan for the USGS Kentucky WSC Sediment Laboratory (Shreve and Downs, 2005).

Samples for chlorophyll-A analysis are pulled directly from the churn splitter. A 100-mL sample is filtered through a glass-fiber filter; a 50-mL sample will occasionally be filtered, particularly for very turbid storm samples. Samples are wrapped in foil and placed immediately in the freezer. Samples for chlorophyll-A are delivered to the laboratory within two weeks of collection. Analysis is performed by the Maryland Department of Health and Mental Hygiene (MD DHMH) Laboratory in Baltimore, Maryland.

B.4 Analytical Methods

Analytical methods for the constituents collected for the Maryland RIM program are documented in Table 2 and described in the USGS National Water-Quality Laboratory documents.

Laboratory Analysis

Water-quality samples collected by the USGS for the Maryland River Input Monitoring Program are analyzed by the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado; the USGS Kentucky WSC Sediment Laboratory in Louisville, Kentucky; and the Maryland Department of Health and Mental Hygiene (MD DHMH) in Baltimore, MD. Analytical techniques employed by the laboratory are documented in Table 2.

Detailed laboratory methods and quality-assurance procedures are described for the NWQL in Mahoney (2005), available at <http://pubs.usgs.gov/of/2005/1263/pdf/OFR2005-1263.pdf>; for the USGS Kentucky Sediment Laboratory in Shreve and Downs (2005), available at <http://pubs.usgs.gov/of/2005/1230/>; and for the MD DHMH at: <http://www.dhmh.state.md.us/labs/pdf/enviroguide02.pdf> (not dated).

B.5 Quality Assurance/Quality Control

Quality assurance and quality control are a significant component of the monitoring program. The quality-assurance effort includes documentation of concentration variability within the cross section, quality assurance of sample-collection techniques and field personnel using field blanks and replicates, and accounting for variability within and among the analyzing laboratories.

Field blanks are collected using certified inorganic blank water (IBW) purchased from the NWQL. A field blank is collected on site using the same sample-collection equipment and procedures that are used to collect the environmental sample. A minimum of one field blank per station per year is collected and analyzed for all

monitored parameters. There may be instances where topical blanks are collected as well, which may not include all parameters typically measured.

Replicate samples are typically collected two times per site per year during varying flow conditions. Quality-control sample results can be obtained from the USGS, MD-DE-DC WSC, at 5522 Research Park Drive, Baltimore, Maryland 21228.

Field quality control is checked during random field audits. The project field manager assures that samples are collected, labeled, and preserved according to standard operating procedures.

Laboratory quality-control methods are documented by each laboratory's quality-assurance documents, and are listed above in section B.4 of this report.

The USGS NWQL is one of several laboratories that participates in the Chesapeake Bay coordinated split-sampling program (CSSP) in which samples are collected from the Potomac River at Key Bridge at Washington, D.C. (USGS Site 01647595) by D.C. Department of the Environment personnel and are processed in triplicate by USGS personnel and submitted to the USGS National Water-Quality-Laboratory in Denver, Colorado. The CSSP was established in June 1989 to establish a measure of comparability between sampling and analytical operations for water-quality monitoring throughout the Chesapeake Bay and its tributaries. Results are forwarded to the water-quality data manager at the Chesapeake Bay program, who performs an analysis to determine if results differ significantly among labs. The USGS typically participates in this program twice per year, and will continue to participate pending availability of funding for this effort.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance

Instrument sensors for field measurements of water temperature, pH, specific conductance, and dissolved oxygen are cleaned and thoroughly inspected between sampling events. If any sensor is not functioning correctly, it is determined whether it is necessary to perform maintenance and/or replace the instrument.

Physical sampling gear is inspected before each use to assure that all parts are intact. Any gear that shows operational deficiency is not used until repairs or replacement is made.

B.7 Instrument Calibration and Frequency

The meters used to determine field parameters are either a YSI 6920 V2 (4-parameter sonde measures water temperature, pH, specific conductance, and dissolved oxygen) or a YSI 600 OMS (a 3-parameter sonde measures water temperature, specific conductance, and turbidity), depending upon which site is visited. Each meter is calibrated prior to the sampling event. Specific instructions for calibration are found in the operating manuals provided with the instrument, and accessed here: <http://www.ysi.com/media/pdfs/YSI-Calibration-Maintenance-Troubleshooting-Tips-6-Series-Sondes-2-8-10.pdf>. Fresh standards are used for calibration prior to each sampling period. The field technician is responsible for appropriate calibration

A calibration record for each instrument and field parameter is maintained in an electronic folder on the USGS MD-DE-DC WSC network and also kept with the sample field sheet. The calibration form serves as documentation for calibration information for each parameter recorded. It is useful in determining drift in a probe, which indicates that maintenance is necessary. The field technician remains aware of questionable performance of any instruments, and determines when it is necessary to perform maintenance and/or replace an instrument.

B.8 Inspection Acceptance Requirements for Supplies and Consumables

The field technician routinely inspects equipment and supplies. The field technician is responsible for determining when supplies and consumables should be discarded. Special attention is paid to the condition of any filtration supplies (tubing, capsule filters, and filtration apparatus) and sampling equipment to assure that they are not contaminated. If contamination is suspected, the supplies are discarded. Any supplies that have exceeded their expiration date are also discarded.

B.9 Data Acquisition

USGS streamflow data is used in the River Input Monitoring program but not directly collected as part of the project. Streamflow data is a necessary data input in the load estimation model. Site summaries of historic streamflow conditions are shown in Table 3. Period of record indicates the period for which there are published discharge values for the USGS station. The annual mean for the period of record is the arithmetic mean of the individual daily-mean discharges for the designated period of record. The highest and lowest daily means are the maximum daily-mean discharge and minimum daily-mean discharge, respectively, for the designated period of record.

Daily-mean discharges are computed by applying the daily mean stages (gage heights) to the stage-discharge curves (James and others, 2003). The USGS provides stage and discharge data for gaging stations on the world wide web (WWW). These data may be accessed at http://waterdata.usgs.gov/nwis/dv?referred_module=sw.

Table 3. Maryland River Input Monitoring and NTN site drainage area and historic streamflow conditions *. [mi², square miles; ft³/s, cubic feet per second]

Period of Record	Drainage area (mi ²)	Annual Mean discharge (ft ³ /s)	Highest Daily Mean discharge (ft ³ /s)	Lowest Daily Mean discharge (ft ³ /s)
<u>Choptank River near Greensboro (01491000)</u>				
Water Year 1948 to 2015	113	140	8,700	0.35
<u>Susquehanna River at Conowingo (01578310)</u>				
Water Year 1968 to 2015	27,000	40,940	1,120,000	269
<u>Patuxent River near Bowie (01594440)</u>				
Water Year 1977 to 2015	348	392	13,700	56
<u>Potomac River at Chain Bridge (01646500)</u>				
Water Year 1930 to 2015	11,560	11,450	426,000	121
<u>Watts Branch at Washington, D.C. (01651800)</u>				
Water Year 1992 to 2015	3.28	4.66	204	0.14
<u>Hickey Run at National Arboretum at Washington, D.C. (01651770)</u>				
Water Year 2013 to 2015	0.99	2.09	97	0.15
<u>Rock Creek at Joyce Road Washington, D.C. (01648010)</u>				
Water Year 2013 to 2015	63.7	86.8	1,930	5.2
<u>Chesterville Branch nr Crumpton, MD (01493112)</u>				
Water Year 1996 to 2015	6.12	8.18	722	1.7

*Source: USGS Water-Year Summary, NWISWEB: <http://nwis.waterdata.usgs.gov/nwis>

B.10 Data Management

All data will be collected using a standardized, site-specific field data sheet (see Attachment A). Field sheets are coded with the site ID (station number), date, collection time, and collector's initials. Field data are entered into the USGS National Water Information System (NWIS) data-management system by technicians who collect the data using standard USGS data entry procedures.

Data analyzed by the MD DHMH (chlorophyll analysis) are sent via hard copy to the RIM Project Field Manager, where they are entered into the USGS database by project staff. The original hard-copy data sheets are maintained and archived at the USGS MD-DE-DC WSC in Baltimore.

Data files are maintained on the USGS computer network and backed up electronically per USGS protocol. The USGS MD-DE-DC WSC in Baltimore stores the archived copies of the field data sheets, laboratory analytical services request (ASR) forms, and the DHMH chlorophyll data sheets per USGS data-archive protocols. Copies of the original data sets are maintained by the Project Field Manager and provided to MD DNR in Excel format. Electronic files with appropriate metadata will be forwarded to the appropriate analysts.

Water-quality data are reviewed when it's received from the laboratory. Summary statistics are calculated and data plots are reviewed to identify anomalies in the data. When anomalies in the field parameters (water and air temperature, pH, specific conductance, dissolved oxygen, barometric pressure) are identified, the data are verified against the original field-data sheet and corrected if necessary. When anomalies in the NWQL-analyzed data are identified, the laboratory analysis may either be repeated (rerun) if the sample is still available (nutrient samples are kept in the laboratory refrigerator and discarded after one month) or the data value verified at the laboratory for transcription errors. Anomalies in the USGS Kentucky Sediment lab-analyzed and the DHMH-analyzed chlorophyll data are noted in the comment field in the data base. Reruns of sediment samples and chlorophyll samples are not possible because the entire sample is used in the initial analysis.

USGS will submit finalized, reviewed discrete water-quality data for the water year directly to the EPA Chesapeake Bay Program via the data upload and evaluation tool (DUET) on an annual basis, per the deliverable schedule listed in the RIM scope of work. Data transfer is delivered by April 15 following the end of the previous water year. Metadata files are linked to the data files that are transferred to MD DNR electronically. Water-quality and streamflow data are also available at the following website: <http://waterdata.usgs.gov/nwis/>.

Quality-control results will be transferred when the QC sample-time issue is resolved. USGS assigns different time stamps on the environmental and QC samples per several national programs' protocol (i.e. NAWQA, NASQAN) as well as USGS data base needs.

B.11 Data Analysis

USGS project staff from the Maryland, Virginia, and Pennsylvania Water Science Centers perform data analysis for load and trend estimation.

Load-Estimation Procedure

Nutrient and suspended-sediment loads for the four Maryland tributary sites will be calculated using the Weighted Regressions on Time, Discharge, and Season (WRTDS) analysis software (Hirsch and others, 2010, Moyer and others, 2012). This approach utilizes an extended period of streamflow and water-quality measurements to predict loads based on the relation of concentration with time, discharge and season. The method utilizes all measurements but weights the values based on nearest values in the dimensions of time, discharge and season. As a result, reported load estimates may fluctuate with periodic updates to the data series. This fluctuation results from newly collected data being included in the analysis and improving the characterization of historical periods. Over time, the load estimates stabilize and will likely show variations of less than 1 percent with subsequent updates.

C. Assessment/Oversight

C.1 Assessment and Response Actions

The USGS quality-assurance officer will conduct random field and office audits to ensure that data collection and data manipulation follow guidelines set forth in the to the quality-assurance plan. A minimum of one field audit will be conducted each year. The field audit will consist of examining all aspects of the field collection for accuracy and adherence to sampling procedures. The field audit will be representative of all sites, but will not necessarily require a visit to each site. A summary report documenting the field activities will be provided. Office audits will be conducted to ensure that all logs are completed and up-to-date, and that proper data management and manipulation is being conducted. The project chief will be immediately notified of any deficiencies and take immediate corrective actions.

The project field manager will continually monitor the logs and records associated with the project to assure that project schedules are being met. The project chief will immediately take any corrective action necessary if project schedules and procedures are being violated. The quality-assurance officer will perform and report on technical system audits and data-quality audits. Peer review of the project design and results will be solicited. Experts in the various field of study will be contacted for comments and suggestions on data analysis and study elements. Data-quality assessments will be conducted to determine whether the assumptions were met.

A USGS WSC Water-Quality Review is held every three years by the USGS Regional Water-Quality Specialist and Regional Staff. Field methods are observed for consistency with USGS protocols, and the WSC database is checked for consistency with field data sheets and published data.

C.2 Reports to Management

Quarterly progress reports are submitted from the USGS to MD DNR to describe quarterly project activities (Attachment D). Any deviations from scheduled project activities will be noted and the effect of these deviations on the final project outcome will be described. Corrective measures will also be suggested. The River Input project field manager (USGS) is responsible for producing and distributing progress reports.

D. Data Validation and Usability

D.1 Data Review, Validation, and Verification

Water-quality data will be verified using a previously developed data quality-control system. Field data are scrutinized during the data-entry phase; laboratory data are reviewed as they are released from the laboratory. Summary statistics are calculated and data plots are examined for outliers or anomalies. When anomalies in the field parameters (water and air temperature, pH, specific conductance, dissolved oxygen, barometric pressure) are identified, the data are verified against the original field-data sheet and corrected if necessary. When anomalies in the laboratory data are identified, the laboratory analysis may either be repeated (rerun) if the sample is still available (nutrient samples are discarded after one month) or the data value verified at the laboratory for transcription errors. The data are corrected in the database if necessary.

Field audits are performed to assure that all data are collected according to standard operating procedures, and that the collection effort is consistent. The USGS Project Field Manager is responsible for performing quality control, or assuring that quality control is performed by appropriate staff.

All field-data sheets and information are thoroughly reviewed prior to data analysis to assure that all data were collected uniformly. Any data that are not collected according to standard operating procedures are examined to determine whether they are representative. All quality-assurance reports are examined prior to data analysis to verify that data were properly and consistently collected. Any deviations in data collection are taken into account during data analysis. All calibration logs are examined to determine how well the measurement instruments

performed. If there appears to be significant drift in instrument performance, the data are adjusted accordingly. All raw data are kept in paper files. Field data are entered into the NWIS database and compared against the original field data sheet for errors. These errors will be corrected. Original (raw) data are retained by the project field manager. The field data sheets will be placed into a site-specific folder. A site-specific sample log is maintained in an Excel spreadsheet, which documents sample date and time, analyses performed, database record numbers, qc performed, and the like. The final verified computerized data set is forwarded to the data analysts.

D.2 Validation and Verification Method

All field technicians use the personal computing field form (PCFF) – an electronic field data sheet – which provides fields to record all physical parameters and cross-section variability data collected with the water-quality sample in electronic format, and includes the information needed for the analytical services request form (ASR). Attachment A shows a paper version of a field form, and Attachment C shows a paper version of the ASR; the electronic version includes the same fields. Data from this form are electronically uploaded to the USGS NWIS database. A printout of uploaded data is then reviewed for accuracy.

A substantial effort is incorporated into the monitoring program to document and ensure quality assurance (QA) and quality control (QC). The quality-assurance effort includes documentation of observed concentration variability within the cross section, sediment transport analysis, quality assurance of sample-collection techniques and field personnel, and the variability within and among the analyzing laboratories. Field quality control is verified during random field audits. The project field manager assures that samples are collected, labeled and preserved in accordance with standard operating procedures. Field blanks are submitted to evaluate the potential for contamination of samples during their collection, processing, and transport.

D.3 Reconciliation with Data-Quality Objectives

Data summaries of mean daily, mean monthly and annual nutrient loads, suspended-sediment loads, and daily mean streamflow will be given to MD DNR for further review and distribution to Chesapeake Bay Resource Managers and researchers.

D.4 Nutrient and Sediment Load Quality Assurance

Estimated nutrient and sediment loads will be computed by WRTDS for the water year in kg/day (concentration units in water-quality-file are mg/L) with associated standard errors (S.E.) and stand errors of prediction (S.E. PRED.). The USGS project chief is responsible for performing quality control through a technical review by colleague and associate USGS staff inside and outside the River Input project.

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Attachment A: Example of information recorded with each USGS water-quality sample

04/2003

U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY NOTES



NWIS RECORD NO _____

STATION NO. _____ SAMPLE DATE ____/____/____ MEAN SAMPLE TIME(CLOCK) _____
 STATION NAME _____ SAMPLE MEDIUM ____ SAMPLE TYPE ____ TIME DATUM ____ (eg. EST, EDT, UTC)
 PROJECT NO. _____ PROJ NAME _____ SAMPLE PURPOSE (71999) ____ PURPOSE OF SITE VISIT (50280) ____
 SAMPLING TEAM _____ TEAM LEAD SIGNATURE _____ DATE ____/____/____
 START TIME _____ GAGE HT _____ TIME _____ GHT _____ TIME _____ GHT _____ TIME _____ GHT _____ END TIME _____ GHT _____

QC SAMPLE COLLECTED? EQUIP BLANK ____ FIELD BLANK ____ SPLIT ____ CONCURRENT ____ SEQUENTIAL ____ SPIKE ____ TRIP BLANK ____ OTHER ____
 NWIS RECORD NOS. _____

LABORATORY INFORMATION

SAMPLES COLLECTED: NUTRIENTS ____ MAJOR IONS ____ TRACE ELEMENTS: FILTERED ____ UNFILTERED ____ MERCURY ____ VOC ____ RADON ____
 TPC ____ (VOL FILTERED ____ mL) TPC ____ (VOL FILTERED ____ mL) PIC ____ (VOL FILTERED ____ mL) DOC ____ ORGANICS: FILTERED ____ UNFILTERED ____
 ISOTOPES ____ MICROBIOLOGY ____ CHLOROPHYLL ____ BOD ____ COD ____ ALGAE ____ INVERTEBRATES ____ FISH ____ BED SED. ____
 SUSP. SED. ____ CONC. SF SIZE RADIOCHEMICALS: FILTERED ____ UNFILTERED ____ OTHER ____ OTHER ____
 LABORATORY SCHEDULES: _____
 LAB CODES: _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____
 COMMENTS: _____ DATE SHIPPED ____/____/____

FIELD MEASUREMENTS

GAGE HT (00065) _____ ft	COND (00095) _____ μ S/cm@25 °C	CARBONATE (00452) _____ mg/L
Q, INST. (00061) _____ cfs MEAS. RATING EST.	TEMP, AIR (00020) _____ °C	HYDROXIDE (71834) _____ mg/L
DIS. OXYGEN (00300) _____ mg/L	TEMP, WATER (00010) _____ °C	E. COLI () _____ col/100mL
BAROMETRIC PRES. (00025) _____ mm Hg	TURBIDITY (61028) _____ ntu	FECAL COLIFORM (31625) _____ col/100mL
DO SAT. (00301) _____ %	ALKALINITY () _____ mg/L	TOTAL COLIFORM (31501) _____ col/100 mL
eH (00090) _____ mvolts	ANC () _____ mg/L	OTHER: _____
pH (00400) _____ UNITS	BICARBONATE (00453) _____ mg/L	OTHER: _____

SAMPLING INFORMATION

Sampler Type (84164) _____ Sampler ID _____ Sample Compositor/Splitter: PLASTIC TEFLON CHURN CONE OTHER _____
 Sampler Bottle/Bag Material: PLASTIC TEFLON OTHER _____ Nozzle Material: PLASTIC TEFLON OTHER _____ Nozzle Size: 3/16" 1/4" 5/16"
 Stream Width: _____ ft mi Left Bank _____ Right Bank _____ Mean Depth: _____ ft Ice Cover _____ % Ave. Ice Thickness _____ in.
 Sampling Points: _____
 Sampling Location: WADING CABLEWAY BOAT BRIDGE UPSTREAM DOWNSTREAM SIDE OF BRIDGE _____ ft mi above below gage _____
 Sampling Site: POOL RIFFLE OPEN CHANNEL BRAIDED BACKWATER Bottom: BEDROCK ROCK COBBLE GRAVEL SAND SILT CONCRETE OTHER _____
 Stream Color: BROWN GREEN BLUE GRAY CLEAR OTHER _____ Stream Mixing: WELL-MIXED STRATIFIED POORLY-MIXED UNKNOWN OTHER _____
 Weather: SKY- CLEAR PARTLY CLOUDY CLOUDY PRECIP- LIGHT MEDIUM HEAVY SNOW RAIN MIST WIND- CALM LIGHT BREEZE GUSTY WINDY EST. WIND SPEED ____
 TEMP- VERY COLD WARM HOT COMMENTS _____
 Sampling Method (82398): EW [10] EDI [20] SINGLE VERTICAL [30] MULT VERTICAL [40] OTHER _____ Stage: STABLE, NORMAL STABLE, HIGH RISING FALLING PEAK
 OBSERVATIONS: _____

COMPILED BY: _____ CHECKED BY: _____ DATE: _____

STN NO _____

METER CALIBRATIONS

TEMPERATURE Meter MAKE/MODEL _____ S/N _____ Thermister S/N _____ Thermometer ID _____

Lab Tested against NIST Thermometer/Thermister? N Y Date: ____/____/____ ± _____ °C

Measurement Location: CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:** _____ °C **REMARK** _____ **QUALIFIER** _____

pH Meter MAKE/MODEL _____ S/N _____ Electrode No. _____ Type: GEL LIQUID OTHER _____

Sample: FILTERED UNFILTERED CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ FT DEEP VERTICAL AVG. OF _____ POINTS

pH BUFFER	BUFFER TEMP	THEORETICAL pH FROM TABLE	pH BEFORE ADJ.	pH AFTER ADJ.	SLOPE	MILLI-VOLTS	BUFFER LOT NO.	BUFFER EXPIRATION DATE	COMMENTS
pH 7									
pH 7									
pH 7									
pH ____									
pH ____									
pH ____									
CHECK pH ____									

TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED?

CALIBRATION COMMENTS:

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **USE:** _____ **UNITS** **REMARK** _____ **QUALIFIER** _____

SPECIFIC CONDUCTANCE Meter MAKE/MODEL _____ S/N _____ Sensor Type: DIP CUP FLOW-THRU OTHER _____

Sample: CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS Temperature compensation: _____

STD VALUE	STD TEMP	SC BEFORE ADJ.	SC AFTER ADJ.	STD LOT NO	STD EXPIRATION DATE	COMMENTS

AUTO
 MANUAL CORR. FACTOR= _____

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:** _____ **µS/cm** **REMARK** _____ **QUALIFIER** _____

DISSOLVED OXYGEN Meter MAKE/MODEL _____ S/N _____ Probe No. _____

Sample: SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS BOD BOTTLE OTHER _____ Stirrer Used? Y N

Air Calibration Chamber in Water _____ Air-Saturated Water _____ Air Calibration Chamber in Air _____ Winkler Titration _____ Other _____

Battery Check: REDLINE _____ RANGE _____ THERMISTER Check? Y N Zero DO Check: Y N Solution Date _____

WATER TEMP °C	BAROMETRIC PRESSURE mm Hg	DO TABLE READING mg/L	SALINITY CORR. FACTOR	DO BEFORE ADJ.	DO AFTER ADJ.

Zero Meter Reading _____ mg/L Adj. to _____ mg/L
 Membrane Changed? N Y Date: ____/____/____ Time: _____
 Barometer Calibrated? N Y Date: ____/____/____ Time: _____

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:** _____ **mg/L** **REMARK** _____ **QUALIFIER** _____

Attachment B₁: USGS NWQL Schedule 1965 for Nutrient Analysis

NWQL Catalog

Schedule 1965

Description: Chesapeake Bay River Inputs Project

Price: \$293.48

Owner: MARYLAND/DELAWARE/DC DISTRICT (NAWQA/WRD)

Analyte▲	Lab Code	Parameter Code	M	CAS Number	RL	Unit	RL Type	C A	Container ID
Inorganic carbon	2608	00688	00127		0.03	mg/L	ltmdl		81 (TPCN)
Total Particulate Carbon (TPC)	2606	00694	COMB6		0.05	mg/L	ltmdl		81 (TPCN)
Organic carbon	2612	00681	OX006		0.23	mg/L	ltmdl		49 (DOC)
Organic carbon	2611	00689	CAL06		0.05	mg/L	mr1		81 (TPCN)
Nitrogen, ammonia as N	3116	00608	00048	7664-41-7	0.010	mg/L	ltmdl	C	54 (FCC)
nitrogen, nitrite	3117	00613	00049	14797-65-0	0.001 0	mg/L	mdl	C	54 (FCC)
nitrogen, nitrite + nitrate	3156	00631	RED01		0.04	mg/L	mdl		54 (FCC)
Total Particulate Nitrogen (TPN)	2607	49570	COMB7	17778-88-0	0.030	mg/L	ltmdl		81 (TPCN)
Total nitrogen (NH ₃ +NO ₂ +NO ₃ +Organic), filtered	2754	62854	CL063	17778-88-0	0.05	mg/L	ltmdl		54 (FCC)
Phosphorus	2331	00666	CL020	7723-14-0	0.003 0	mg/L	ltmdl		54 (FCC)
phosphorus, phosphate, ortho	3118	00671	00048	14265-44-2	0.004	mg/L	ltmdl	C	54 (FCC)
Phosphorus	2333	00665	CL021	7723-14-0	0.004	mg/L	ltmdl		60 (WCA)
Residue	169	00530	SLD04		15	mg/L	mr1		57 (SUSO)
residue, volatile	49	00535	SLD05		10	mg/L	mr1		57 (SUSO)
Silica	3121	00955	CL151	7631-86-9	0.06	mg/L	ltmdl		55 (FU)

CAS Registry Number® is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services.

Values of "C" in the C A column denote NELAP Certified analytes

References

- EPA 440.0**
Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis, Revision 1.4, September 1997, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development
Method ID: 440.0
- [WRIR 03-4174](#)
Patton, C.J., Kryskalla, J.R., Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory, Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorus in Water, Water-Resources Investigations Report 03-4174, 33p.
Method ID: I-2650-03
- [U.S. Geological Survey Techniques and Methods, book 5, chap. B8](#)

Patton, C. J., and Kryskalla, J. R., 2011, Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods: U.S. Geological Survey Techniques and Methods, book 5, chap. B8

Method ID: I-2547-11

4. [TWRI B5-A1/89](#)

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Method ID: I-3765-89 , I-2700-85 , I-3767-89

5. **EPA 365.1**

Determination of Phosphorus by Semi-Automated Colorimetry Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples

Method ID: 365.1

6. [OFR 92-480](#)

Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of dissolved organic carbon by uv-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.

Method ID: O-1122-92

7. [OFR 93-125](#)

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Method ID: I-2540-90 , I-2525-89 , I-2601-90 , I-2542-89 , I-2522-90 , I-2606-89

8. [OWQ Tech Memo 2000.08](#)

New Method for Particulate Carbon and Particulate Nitrogen, June 1, 2000

9. [OWQ Tech Memo 2000.08](#)

New Method for Particulate Carbon and Particulate Nitrogen, June 1, 2000

10. [Memo - method approval announcement \(July 2, 2003\)](#)

Approval of a Water Quality Analytical Method for the Determination of Nitrogen and Phosphorus in Whole and Filtered Water by the National Water Quality Laboratory

Method ID: I-2650-03

11. [Memo -- USEPA Approval for nationwide use of ATP method](#)

Telliard, W.A., USEPA, Director of Analytical Methods, Engineering and Analysis Division

12. [OWQ TM 2009.03](#)

Potential Bias in Alkaline Persulfate Analysis of Total Nitrogen in Whole Water Samples and Recommendations for Quantifying Bias in Whole Water Samples, Office of Water Quality Technical Memorandum 2009.03

Attachment B₂: USGS NWQL Schedule 2580 for Nutrient Analysis

NWQL Catalog

Schedule 2580									
Add To Favorites Sample, Container, and Field Information									
Description: MD.Bell.nutrients, TPCN, and metals Price: \$275.70 Owner: USGS - MARYLAND DISTRICT, MD									
Analyte▲	Lab Code	Parameter Code	M	CAS Number	RL	Unit	RL Type	C A	Container ID
Cadmium	1788	01025	PLM43	7440-43-9	0.06	ug/L	DLBLK		53 (FA)
Total Particulate Carbon (TPC)	2606	00694	COMB6		0.05	mg/L	ltmdl		81 (TPCN)
Organic carbon	2612	00681	OX006		0.23	mg/L	DLDQC		49 (DOC)
Chloride	1571	00940	IC022	16887-00-6	0.02	mg/L	DLDQC	C	55 (FU)
Copper	3128	01040	PLM10	7440-50-8	0.4	ug/L	DLBLK		53 (FA)
ICP Mass Spectrometry (ICPMS) setup	2181	L2181				unsp	mrl		53 (FA)
Lead	1792	01049	PLM43	7439-92-1	0.04	ug/L	DLBLK		53 (FA)
Nitrogen, ammonia	3116	00608	SHC02	7664-41-7	0.01	mg/L	DLDQC	C	138 (FCC or FCCVT)
nitrogen, nitrite	3117	00613	DZ001	14797-65-0	0.00 1	mg/L	DLDQC	C	138 (FCC or FCCVT)
nitrogen, nitrite + nitrate	3157	00631	RED02		0.01	mg/L	DLDQC		138 (FCC or FCCVT)
Total Particulate Nitrogen (TPN)	2607	49570	COMB7	17778-88-0	0.03 0	mg/L	ltmdl		81 (TPCN)
Total nitrogen (NH ₃ +NO ₂ +NO ₃ +Organic), filtered	2754	62854	CL063	17778-88-0	0.05	mg/L	DLDQC		54 (FCC)
Phosphorus	2331	00666	CL020	7723-14-0	0.00 3	mg/L	DLDQC		54 (FCC)
phosphorus, phosphate, ortho	3118	00671	PHM01	14265-44-2	0.00 4	mg/L	DLDQC	C	138 (FCC or FCCVT)
Phosphorus	2333	00665	CL021	7723-14-0	0.00 4	mg/L	DLDQC	C	60 (WCA)
Residue	169	00530	SLD04		15	mg/L	mrl		55 (SUSO)
specific conductance, laboratory	69	90095	WHT03		5	uS/cm	mrl		55 (RU)
Zinc	3138	01090	PLM10	7440-66-6	4	ug/L	DLBLK		53 (FA)
Lab Code 69 may only be deleted when the field conductivity value is provided.									
<i>CAS Registry Number® is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services.</i> <i>Values of "C" in the C A column denote NELAP Certified analytes</i>									
Excel Format					Sample, Container, and Field Information				
References									
1. TMR Book 5, Sec B, Chap 1 Garbarino. J.R.. Kanaav. L.K.. and Cree. M.E.. 2005. Determination of elements in natural-water. biota.									

sediment and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, sec. B, chap.1, 88 p.

Method ID: I-2020-05

2. **EPA 365.1**
Determination of Phosphorus by Semi-Automated Colorimetry Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples
Method ID: 365.1
3. **OFR 93-125**
Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.
Method ID: I-2540-90 , I-2525-89 , I-2601-90 , I-2542-89 , I-2522-90 , I-2606-89
4. **EPA 440.0**
Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis, Revision 1.4, September 1997, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development
Method ID: 440.0
5. **WRIR 03-4174**
Patton, C.J., Kryskalla, J.R., Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory , Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorus in Water, Water-Resources Investigations Report 03-4174, 33p.
Method ID: I-2650-03
6. **TWRI B5-A1/89**
Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
Method ID: I-2781-85 , I-2057-85 , I-3765-85
7. **U.S. Geological Survey Techniques and Methods, book 5, chap. B8.**
Patton, C. J., and Kryskalla, J. R., 2011, Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods: U.S. Geological Survey Techniques and Methods, book 5, chap. B8.
Method ID: I-2548-11
8. **Memo - Method approval announcement**
Approval of a Water Quality Analytical Method for the Determination of Elements in Natural Water, Biota, Sediment, and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry, November 3, 2005 (revised)
9. **OFR 92-480**
Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of dissolved organic carbon by uv-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.
Method ID: O-1122-92
10. **Memo - method approval announcement (July 2, 2003)**
Approval of a Water Quality Analytical Method for the Determination of Nitrogen and Phosphorus in Whole and Filtered Water by the National Water Quality Laboratory
Method ID: I-2650-03
11. **OWQ Tech Memo 2000.08**
New Method for Particulate Carbon and Particulate Nitrogen, June 1, 2000
12. **Memo -- USEPA Approval for nationwide use of ATP method**
Telliard, W.A., USEPA, Director of Analytical Methods, Engineering and Analysis Division
13. **OWQ TM 2009.03**
Potential Bias in Alkaline Persulfate Analysis of Total Nitrogen in Whole Water Samples and Recommendations for Quantifying Bias in Whole Water Samples, Office of Water Quality Technical Memorandum 2009.03

Attachment C: NWQL Analytical Services Request (ASR) Form

U.S. GEOLOGICAL SURVEY – NWQL ASR

THIS SECTION MANDATORY FOR SAMPLE LOGIN

NWIS RECORD NUMBER SAMPLE TRACKING ID	<table border="1" style="width:100%; text-align: center;"> <tr><td>M</td><td>D</td></tr> </table> User Code	M	D	<table border="1" style="width:100%; text-align: center;"> <tr><td>2</td><td>4</td><td>2</td><td>7</td><td>B</td><td>4</td><td>8</td><td>Ø</td><td>1</td></tr> </table> Project Account	2	4	2	7	B	4	8	Ø	1	LAB USE ONLY NWQL LABORATORY ID					
M	D																		
2	4	2	7	B	4	8	Ø	1											
<table border="1" style="width:100%; text-align: center;"> <tr><td>0</td><td>1</td><td>5</td><td>7</td><td>8</td><td>3</td><td>1</td><td>0</td></tr> </table> STATION ID	0	1	5	7	8	3	1	0	<table border="1" style="width:100%; text-align: center;"> <tr><td>2</td><td>0</td><td>0</td></tr> </table> Begin Date (YYYYMMDD)	2	0	0	<table border="1" style="width:100%; text-align: center;"> <tr><td> </td><td> </td></tr> </table> Begin Time			<table border="1" style="width:100%; text-align: center;"> <tr><td>9</td></tr> </table> Medium Code	9	<table border="1" style="width:100%; text-align: center;"> <tr><td>9</td></tr> </table> Sample Type	9
0	1	5	7	8	3	1	0												
2	0	0																	
9																			
9																			
Brenda Majedi (443) 498-5227 Contact Phone Number			blfeit@usgs.gov Contact Email																

SITE / SAMPLE / SPECIAL PROJECT INFORMATION (Optional)

24 State	County	Geologic Unit Code	H Analysis Status*	9 Analysis Source*	Hydrologic Condition*	9 Hydrologic Event*	Chain of Custody	Sample Set
NWQL Proposal Number	NWQL Contact Name	NWQL Contact Email	Program/Project					

Station Name: SUSQUEHANNA R. @CONOWINGO, MD Field ID: _____

Comments to NWQL: _____

Hazard (please explain): _____

ANALYTICAL WORK REQUESTS: SCHEDULES AND LAB CODES (CIRCLE A=add D=delete)

SCHED 1: 1965 SCHED 2: _____ SCHED 3: _____ SCHED 4: _____ SCHED 5: _____ SCHED 6: _____

Lab Code: _____				
Lab Code: _____ A D				
Lab Code: _____ A D				

SHIPPING INFORMATION (Please fill in number of containers sent)

___ ALF	___ COD	___ FA	___ FCN	___ IQE	___ IRM	___ RA	___ RU	___ SUR	<u>1</u> TPCN
___ BGC	___ CRB	___ FAM	<u>1</u> FU	___ IQL	___ MBAS	___ RAM	___ RUR	<u>1</u> SUSO	___ UAS
___ C18	___ CU	___ FAR	___ FUS	___ IQM	___ OAG	___ RAR	___ RURCT	___ TBI	<u>1</u> WCA
___ CC	___ CUR	___ FCA	___ GCC	___ IRE	___ PHE	___ RCB	___ RURCV	___ TBY	___
___ CHY	<u>1</u> DOC	<u>1</u> FCC	___ GCV	___ IRL	___ PIC	___ RCN	___ RUS	___ TOC	___

NWQL Login Comments: _____

Collected by: Brenda Majedi Phone No. (410) 238-4227 Date Shipped: _____

FIELD VALUES

Lab/P Code	Value	Remark
21/00095		
Specific Conductance uS/cm @ 25 deg C		
51/00400		
pH Standard Units		

EXAMPLE

Chesapeake Bay River Input Monitoring Program

Quarterly Progress Report

January 1, 2017 to March 31, 2017

Monitoring Sites:

- Susquehanna River at Conowingo Dam, Maryland (01578310)
- Potomac River at Chain Bridge, District of Columbia (01646580)
- Patuxent River near Bowie, Maryland (01594440)
- Choptank River near Greensboro, Maryland (01491000)

Internal Acct #s: B4800, B4801

Start Date: July 1985

Completion Date: Ongoing

Project Personnel:

Joel Blomquist, Hydrologist
Brian Banks, Hydrologic Technician
Deborah Bringman, Hydrologic Technician
David Brower, Hydrologic Technician
Brenda Majedi, Hydrologic Technician

Project Objectives:

- Determine the ambient concentrations of nutrients and suspended sediment collected over a range in flow conditions near the point of tidal influence of four major Maryland tributaries to the Chesapeake Bay: the Susquehanna, Potomac, Patuxent and Choptank Rivers.
- Estimate monthly, and annual loading of nutrients and suspended sediment entering the Chesapeake Bay from the non-tidal portions of the Susquehanna, Potomac, Patuxent and Choptank Rivers.
- Identify trends in constituent concentration data at the four tributary stations.

Progress this Quarter:

- Reviewed and approved WY 2016 discrete water-quality data were transmitted directly to the EPA Chesapeake Bay Program Office (CBPO) via the data upload and evaluation tool (DUET). Email documentation regarding successful data transmission was sent to MD DNR.
- Reviewed and approved WY 2016 mean-daily discharge data were transmitted in Excel format to MD DNR in March 2017.
- WY 2016 continuous water-quality data were approved for USGS site ID 01579550 (Susquehanna River near Darlington, MD) for water temperature, specific conductance, and turbidity; nitrate data are currently in review.
 - Operation and maintenance of the continuous water-quality instrumentation continued during this reporting period. The data are displayed in near real time at the following webpage:
<http://waterdata.usgs.gov/usa/nwis/uv?01579550>.
- WY 2016 continuous water-quality data were approved for USGS site ID 01646500 (Potomac River at Little Falls) for water temperature, specific conductance, pH, dissolved oxygen, and turbidity; nitrate data are currently in review.
 - Operation and maintenance of the continuous water-quality instrumentation continued during this reporting period. Continuous water-quality data for this station is funded by a separate USGS program. The data are displayed in near real time at the following webpage:
<http://waterdata.usgs.gov/md/nwis/uv?01646500>
- Provisional water-quality data collected for the December 2016 coordinated split-sample program was provided to the CBPO water-quality data manager.
- Fixed-frequency and stormflow sample collection continued at each site per the scope of work. See summary table below which lists samples collected at each site this reporting period.
 - Monthly fixed-interval samples were collected at all four sites in January, February, March 2017, including sample collection for the USGS National Water Quality Network (NWQN) program at the Susquehanna River and the Potomac River. The USGS NWQN program provides support for the fixed-frequency sample collection and analysis at the Susquehanna and Potomac Rivers.
 - Note that at the Susquehanna River at Conowingo, two fixed-frequency samples were collected during the months of January, February, and March, and at the Potomac River at Chain Bridge, two fixed-frequency samples were collected during the months of February and March, per NWQN sampling plan.
 - Stormflow samples were collected at all four sites this reporting period. Storm samples collected on the day of the monthly fixed-frequency sample day are counted as fixed-frequency samples, not storm samples. They are listed in the *FF Storm Impacted* column but not counted in the Total Samples Collected column.
 - Quarterly major ions were collected at the Choptank station during this reporting period. The USGS NWQN program provides support for major-ion analyses each month at the Susquehanna and Potomac River sites.
 - Sample collection continued at the Potomac, Susquehanna, Patuxent, and Choptank River sites for the analysis of nitrogen isotopes and fluorescence by UMBC, and for bacterial DNA at the Susquehanna River.

Sampling Summary: January 1, 2017 to March 31, 2017

Site	Monthly FF	<i>(FF Storm Impacted)</i>	Storm	QC	Total Samples Collected
Susquehanna at Conowingo, MD (01578310)	6	--	3	2	11
Potomac at Chain Bridge, D.C. (01646580)	5	(1)	2	2	9
Patuxent near Bowie, MD (01594440)	3	--	2	1	6
Choptank near Greensboro, MD (01491000)	3	--	3	1	7

QC, quality control. (Not all parameters analyzed for QC samples.)

FF, Fixed-frequency sample.

Note: Total Samples Collected does not include the *FF storm-impacted* samples, as these are already included in the monthly FF.

Plans for Next Quarter:

- Provide to MD DNR the MD RIM Scope of Work and agreement for SFY 2018.
- Provide to DNR the monthly and annual 2016 load and trend computations in May, and updated loads by mid July 2017, per scope of work.
- Review the RIM QAPP for state fiscal year 2018; update as needed, and send signature page to MD DNR.
- Collect monthly fixed-frequency samples and stormflow samples at all four sites, including sample collection for the USGS NWQN programs at the Susquehanna River and the Potomac River near Chain Bridge, respectively, in April, May, and June 2017. Major ion analysis will continue as well.
 - Twice-monthly sample collection will occur at the Susquehanna River site through May 2017, and at the Potomac River at Chain Bridge through July 2017, per the NWQN sampling plan.
- If flow conditions warrant, samples will be collected for the lower Susquehanna reservoirs suspended-sediment characterization study.
- Continue operation and maintenance of the water-quality instrumentation at the Susquehanna River at Darlington, MD and at the Potomac River at Little Falls.
- Participate in the Chesapeake Bay Coordinated Split Sampling Program in June 2017. USGS participates in this program twice per calendar year, usually in June and December.
- Continue to maintain gaging-station equipment required for real-time stage-discharge data displayed to the public.

Attachment E: USGS DUET METHOD LOOKUP TABLE

Look up table to correlate parmcode and method code to a DUET method code. The nulls are parm/meth combinations

parm_meth_lu

USGS_pcode	USGS_parm_nm	USGS_meth_cd	USGS_meth_nm	DUET_PARAMETER	DUET_METHOD	DUET_TITLE
00010	Temperature, water	THM01	Temperature, water, thermistor	WTEMP	F01	IN-SITU THERMISTOR
00061	Discharge, instant.	QADCP	Disch., meas., ADCP moving boat	FLOW_INS	F01	STREAM FLOW; INSTANTANEOUS
00061	Discharge, instant.	QSCMM	Disch., meas., midsection	FLOW_INS	F01	STREAM FLOW; INSTANTANEOUS
00061	Discharge, instant.	QSTGQ	Discharge, stg-disch rating	FLOW_INS	F01	STREAM FLOW; INSTANTANEOUS
00095	Specific cond at 25C	SC001	Specific conductance sensor	SPCOND	F01	IN-SITU SPECIFIC CONDUCTANCE AT 25 C
00300	Dissolved oxygen	LUMIN	Diss oxygen, luminescence sensor	DO	F04	IN-SITU DISSOLVED OXYGEN; OPTICAL DO PROBE
00300	Dissolved oxygen	MEMBR	Diss oxygen, membrane electrode	DO	F01	IN-SITU MEMBRANE ELECTRODE
00400	pH	EL003	pH, wu, field, electrometry	PH	F01	IN-SITU ELECTRODE METHOD
00400	pH	PROBE	pH, field, electrometric	PH	F01	IN-SITU ELECTRODE METHOD
00530	Suspended solids	SLD04	Sus solids, wat, 105C,wt (NWQL)	TSS	L01	GRAVIMETRIC; DRIED AT 103-105 C
00535	LOI of susp. solids	SLD05	LOI from suspended solids,weight	VSS	L01	GRAVIMETRIC; IGNITION AT 550

						C
00608	Ammonia, wf	00048	Nutrients, wf, color, DA	NH4F	L02	
00613	Nitrite, wf	00049	Nutrients, wf, NaR, colorimetric	NO2F	L01	
00625	NH3+orgN, wu	KJ008	NH4+org-N, wu, WCA, kjeldahl, CF	TKNW	D01	DATABASE CALCULATED TKNW - METHOD 1
00631	NO3+NO2, wf	CL048	Nutrients, Cd reduct, color	NO23F	L01	COLORIMETRIC; AUTOMATED CADMIUM REDUCTION
00631	NO3+NO2, wf	RED01	NO3+NO2, wf, FCC,NaR, DA	NO23F	L03	ENZYMATIC NITRATE METHOD
00631	NO3+NO2, wf	RED02	NO3+NO2, wf, FCC,NaR, DA, LL	NO23F	L03	ENZYMATIC NITRATE METHOD
00665	Phosphorus, wu	AKP01	Nutrients, wu, WCA,persulfate,CF	TP	L04	ALKALINE PERSULFATE DIGESTION AND EPA 365.1
00665	Phosphorus, wu	CL021	P, wu, WCA, persulfate, CF	TP	L04	ALKALINE PERSULFATE DIGESTION AND EPA 365.1
00666	Phosphorus, wf	CL020	P, wf, FCC, persulfate, CF	TDP	L01	ALKALINE PERSULFATE WET OXIDATION + EPA365.1OR EPA 365
00671	Orthophosphate, wf	00048	Nutrients, wf, color, DA	PO4F	L01	
00681	Organic carbon, wf	OX006	DOC,0.45um cap,acid,persulfateIR	DOC	L03	UV OR HEATED PERSULFATE OXIDATION
00688	Inorg carbon, ss,total	00127	PIC	PIC	L01	PARTICULATE INORGANIC CARBON

00689	Organic carbon, ss,t	CAL06	POC, calculated			
00694	Total carbon, ss	COMB6	TPC, GFF, combustion	PC	L01	PARTICULATE CARBON (inorg+organic)
00940	Chloride, wf	IC022	Anions, wf, IC			
00940	Chloride, wf	IC024	Anions, LIS wf, IC			
00945	Sulfate, wf	IC022	Anions, wf, IC			
00945	Sulfate, wf	IC024	Anions, LIS wf, IC			
00955	Silica, wf	CL151	Silica, wf, DA	SIF	L01	COLORIMETRIC; AUTOMATED; MOLYBDENUM BLUE
00955	Silica, wf	PLA11	Metals, wf, ICP-AES (NWQL)	SIF	L01	COLORIMETRIC; AUTOMATED; MOLYBDENUM BLUE
32211	Chlorophyll a, phyto,spec		ug/l	CHLA	L01	ACTIVE CHLOROPHYLL-A
63676	Turbidity, NephRatio	TS098	HACH, sensor model 2100 AN, R-On	TURB_NTRU	L01	
63680	Turbidity, Nephelom	TS085	YSI Environmental sensor	TURB_FNU	L01	
63680	Turbidity, Nephelom	TS087	YSI Environmental, sensor 6136	TURB_FNU	L01	
70300	Diss solids dry@180C	ROE10	ROE, wf, 180C, by weight (NWQL)	TDS	L01	TOT. DISSOLVED SOLIDS; GRAVIMETRIC; DRIED AT 180 C
70331	Sus sed <0.0625mm,sd	SED02	Dry sieve	SSC_%FINE	D01	PERCENT OF SUSPENDED SEDIMENT PARTICLES PASSING THROUGH 0.062 MM SIEVE
70331	Sus sed <0.0625mm,sd	SED30	Wet sieve	SSC_%FINE	D01	PERCENT OF SUSPENDED SEDIMENT

						PARTICLES PASSING THROUGH 0.062 MM SIEVE
80154	Suspnd sedmnt conc	SED10	Sediment conc by filtration	SSC_TOTAL	L01	GRAVIMETRIC FILTRATION METHOD; DRIED AT 90-105
80154	Suspnd sedmnt conc	SED16	Sediment conc from size analysis	SSC_TOTAL	L02	GRAVIMETRIC EVAPORATION METHOD; DRIED AT 90-105 DEGREES C