

CHESAPEAKE BAY WATER-QUALITY MONITORING PROGRAM

MARYLAND RIVER INPUT NUTRIENT AND SEDIMENT LOADING TRENDS COMPONENT

QUALITY-ASSURANCE PROJECT PLAN

JULY 1, 2008 to JUNE 30, 2009

**MARYLAND DEPARTMENT OF NATURAL RESOURCES
RESOURCE ASSESSMENT SERVICE**

**IN COOPERATION WITH THE
U.S. GEOLOGICAL SURVEY**

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QUALITY-ASSURANCE PROJECT PLAN

for the

Maryland River Input Monitoring Program

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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 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;
- 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.

A.2 Distribution List

This QAPP will be distributed to the following project participants:

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A.3 Project/Task Organization

Joel Blomquist, USGS, is the Project Manager for the Maryland River Input Monitoring Program and is responsible for the technical design, operation, and execution of the program 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.

J. Shermer Garrison, MD DNR, Tidewater Ecosystem Assessment serves as the Project Coordinator for the Maryland River Input Monitoring Project. He is tasked with assuring that all project commitments, the project timetable, and deliverables are completed.

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.

Cherie V. Miller is the USGS MD-DE-DC Water Science Center (WSC) Water-Quality Specialist. As a quality-assurance officer, she is tasked with conducting field audits and reviewing reports. While these are regular

responsibilities of the USGS WSC Water-Quality Specialist, she may recommend additional quality-control activities to the USGS Project Manager if necessary. Her responsibilities are generally limited to activities in the MD-DE-DC WSC, and she 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 will lead 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 monitoring 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.

A.5 Project/Task Description

At each monitoring station, water-quality samples that are representative of the entire river cross section are collected to determine concentrations of selected nutrient species and suspended sediment in the river. Samples for water-quality analysis are collected on a monthly 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 (Wilde and others, 1999, <http://water.usgs.gov/public/owq/FieldManual/index.html>) 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.

Samples for water-quality analysis are collected during base-flow conditions on a monthly basis as well as during stormflow events. A project field data sheet is completed for each sample (Attachment A). Data on the field sheet will be entered into the USGS National Water Information System (NWIS) data management system and checked for typing errors. Water-quality data are reviewed on a monthly basis. Provisional WY 2008

streamflow, nutrient, and suspended-sediment concentration data for each monitoring station will be forwarded to J. Shermer Garrison at MD DNR by January 15, 2009. Provisional WY 2004-2008 monthly and annual nutrient and suspended-sediment loads for each monitoring station will be forwarded to J. Shermer Garrison by April 15, 2009. A final WY 2008 water-quality concentration data set, and revised (considered final) water year 2004, and interim WY 2005-2008 mean-monthly and annual nutrient and sediment loads will be forwarded on CD-ROM to J. Shermer Garrison by June 30, 2009. Quarterly progress reports describing field and other project activities and issues will also be submitted to J. Shermer Garrison. Additionally, data interpretation of 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

This study 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 Maryland RIM program. 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. 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://www.dhmh.state.md.us/labs/pdf/enviroguide02.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 entered into the USGS NWIS data management system by the technicians who collect the data. These data are provided to MD DNR in hard copy in the form of tables and data summaries. Electronic data on CD-ROM are submitted with the final deliverables, as listed in section A.5.

Water-quality samples are submitted for nutrient analysis to the USGS NWQL in Denver, Colorado. A customized laboratory schedule – NWQL Schedule 1965 (Attachment B) – is requested for each RIM sample submitted. Suspended sediment is analyzed at the USGS Sediment Laboratory in Louisville, Kentucky; and chlorophyll-A 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 records, including calibration information, are archived at the USGS MD-DE-DC WSC in fireproof cabinets, as per USGS protocol.

A web site has been created to provide detailed information about the 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, in cooperation with the USGS, to quantify nutrient and suspended-sediment loads entering the Chesapeake Bay from four tributaries to the Bay and 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 is based on the requirements of the load-computation model. The long-term sampling record (over 20 years of data) at the four River Input sites (Susquehanna, Potomac, Patuxent, and Choptank Rivers) permits fewer samples to be collected each year to characterize nutrient and suspended-sediment loads for the modeling process. Water-quality samples are collected on a monthly basis and during varying stormflow conditions 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 location of the monitoring sites and drainage area information are presented in table 1.

Table 1. Location of the Maryland River Input Monitoring water-quality stations.

Station Name	USGS Station	Bay Program Station	Latitude deg-min-sec	Longitude deg-min-sec	Drainage (sq. mi.)
Susquehanna River at Conowingo Dam, MD	01578310	CB1.0	39-39-28	76-10-29	27,100
Potomac at Chain Bridge River, D.C.	01646580	TF 2.0	38-55-46	77-07-02	11,570
Patuxent River nr. Bowie, MD	01594440	Near TF1.0	38-57-21	76-41-36	348
Choptank River nr. Greensboro, MD	01491000	ET5.0	38-59-50	75-47-10	113

B.2 Sampling Method

USGS personnel collect all water-quality samples at each of the four Maryland RIM stations in accordance with Chapter A4 of the USGS National Field Manual for the Collection of Water Quality Data (Wilde and others, 1999).

Water-quality samples are collected during base-flow conditions on a monthly 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 base-flow and 5-15 stormflow samples are collected at each site per year; stormflow sample collection depends largely upon hydrologic and meteorologic conditions. The average stormflow coverage is three to five samples per season per site. 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. Flood-stage events are predicted through weather forecasts and by remote monitoring of river stage from the USGS offices in Baltimore, Maryland and Dover, Delaware.

Water-quality samples are collected during base-flow conditions at the Susquehanna, Potomac, and Patuxent Rivers using a stainless-steel weighted-bottle sampler, and at the Choptank River using either a DH-81 isokinetic sampler or a dip bottle depending on river stage conditions. The weighted-bottle sampler holds a one-liter bottle made of Teflon, polyethylene, or glass. A prewashed one-liter small-neck (one-inch opening) polyethylene bottle is usually used with the weighted-bottle sampler. A one-liter Teflon bottle is used with the DH-81.

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. 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. Samples are collected along the width of the stream, and composited into a polyethylene churn splitter (a Teflon churn splitter is used at the Susquehanna and Potomac Rivers), which is a device that homogenizes the water-sediment mixture. Subsamples for laboratory analysis are filled from the churn splitter. The exception is for samples collected for analysis of dissolved organic carbon (DOC), particulate carbon (TPC), and particulate nitrogen (TPN), for which a one-liter

glass-baked bottle is used. Samples for these analytes are collected at the river at the center of flow; subsamples for DOC, TPC, and TPN analysis are filtered from this bottle.

Samples for suspended-sediment analysis are collected from the churn splitter during base-flow and stormflow conditions. However, periodically during stormflow conditions, samples may also be collected directly from the river, bypassing the churn splitter, and sent directly to the laboratory for analysis. This is mainly done for quality-control purposes in order to determine the comparability of suspended-sediment concentration collected directly from the river to those samples collected from the churn splitter.

During stormflow conditions, water-quality samples are collected using either a weighted-bottle sampler (at the Susquehanna and Potomac Rivers), or a 35-pound DH-95 or a 65-pound D-95 isokinetic sampler (at the Patuxent and Choptank Rivers). These samplers are composed of an aluminum body with Teflon fins, and are fitted with a one-liter Teflon bottle). Sampler selection is site dependent.

Susquehanna River

USGS personnel collect water samples from the Susquehanna River at the Conowingo Dam in Conowingo, Maryland. Base-flow and stormflow samples are collected using the equal discharge increment method with the stainless-steel weighted-bottle sampler fitted with a one-liter (two-inch mouth) polyethylene 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 currently not allowed because of safety 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. Twelve samples will be collected in fiscal year 2009; some months have semi-monthly sample collection.

Potomac River

USGS personnel collect water samples from the Potomac River at Chain Bridge in Washington, D.C. using the EWI method. Water-quality samples are collected using a stainless-steel weighted-bottle sampler fitted with a one-liter (two-inch mouth) polyethylene 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 samples cannot be collected at Chain Bridge because of flow conditions. 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 polyethylene 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.

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 5.0-ft or a discharge of greater than 20,000 cubic feet per second (cfs or ft³/s).

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.

Patuxent River

USGS personnel collect water samples at the Patuxent River at Governors Bridge on Governors Bridge Road in Bowie, Maryland. Cross-sectional, depth-integrated water-quality samples are collected manually during base-flow and stormflow conditions at ten sections along the bridge. Base-flow samples are collected using a stainless-steel weighted bottle sampler fitted with a one-liter (one-inch mouth) polyethylene bottle suspended by a polyethylene rope.

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-ft 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 at Christian Park located at the end of Red Bridges Road in Greensboro, Maryland. 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.

Base-flow samples at the Choptank River are collected by wading in the river, using the DH-81 isokinetic sampler fitted with a one-liter Teflon bottle. Samples are collected at ten 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 polyethylene bottle filled manually.

During stormflow events, sampling is performed with a DH-95 or a D-95 isokinetic sampler operated from a cablecar along the cableway that traverses the river. Occasionally, storm samples will be collected about 100 feet downstream of the cableway when stream conditions are wadeable (gage height of about 3.25 feet). A storm event on the Choptank River near Greensboro is operationally defined as a USGS gage height of greater than 4.0-ft or a discharge of greater than 400 cubic feet per second (cfs or ft³/s), or below this threshold after a runoff event following a dry spell.

Constituents Monitored

The Maryland River Input Monitoring program focuses on quantifying the water quality and loads of major nutrient species and suspended sediment from the nontidal portion of the Susquehanna, Potomac, Patuxent, and Choptank Rivers. Chemical parameters monitored for the program are listed below and are shown in Figures 1 through 4. The parameter names and codes on the figures are those used by the USGS National Water Quality Laboratory. Analytical methods for these constituents are shown in table 2.

<u>Parameter</u>			<u>Method</u>
TBD	TN	Total nitrogen	calculated = TDN + TPN
49570	TPN	Total particulate nitrogen	measured by LC-2607 at NWQL
62854	TDN	Total dissolved nitrogen	measured by LC-2754 at NWQL
00608	NH3	Ammonia, dissolved	measured by LC-1976 at NWQL
00613	NO2	Nitrite, dissolved	measured by LC-1977 at NWQL
00618	NO3	Nitrate, dissolved	calculated = NO23 - NO2 at NWQL
00631	NO23	Nitrite plus nitrate, dissolved	measured by LC-1975 at NWQL
00665	TP	Total phosphorus	measured by LC-2333 at NWQL
00666	TDP	Total dissolved phosphorus	measured by LC-2331 at NWQL
00671	PO4	Ortho-phosphorous, dissolved	measured by LC-1978 at NWQL
00681	DOC	Dissolved organic phosphorus	measured by LC-2612 at NWQL
00694	TPC	Total particulate carbon	measured by LC-2606 at NWQL
00688	PIC	Particulate inorganic carbon	measured by LC-2608 at NWQL
00689	POC	Particulate organic carbon	measured by LC-2611 at NWQL
00530	TSS	Total suspended solids	measured by LC-169 at NWQL
00535	VSS	Volatile suspended solids	measured by LC-49 at NWQL
80154	SSC	Suspended-sediment conc.	measured at <i>USGS Kentucky sed lab</i>
70331	s-fine	sand-fine fraction, susp. sediment	measured at <i>USGS Kentucky sed lab</i>
00955	Silica	Silica, dissolved as SiO ₂	measured by LC-56 at NWQL
32211	Chlo-a	Chlorophyll A	measured at <i>DHMH</i>

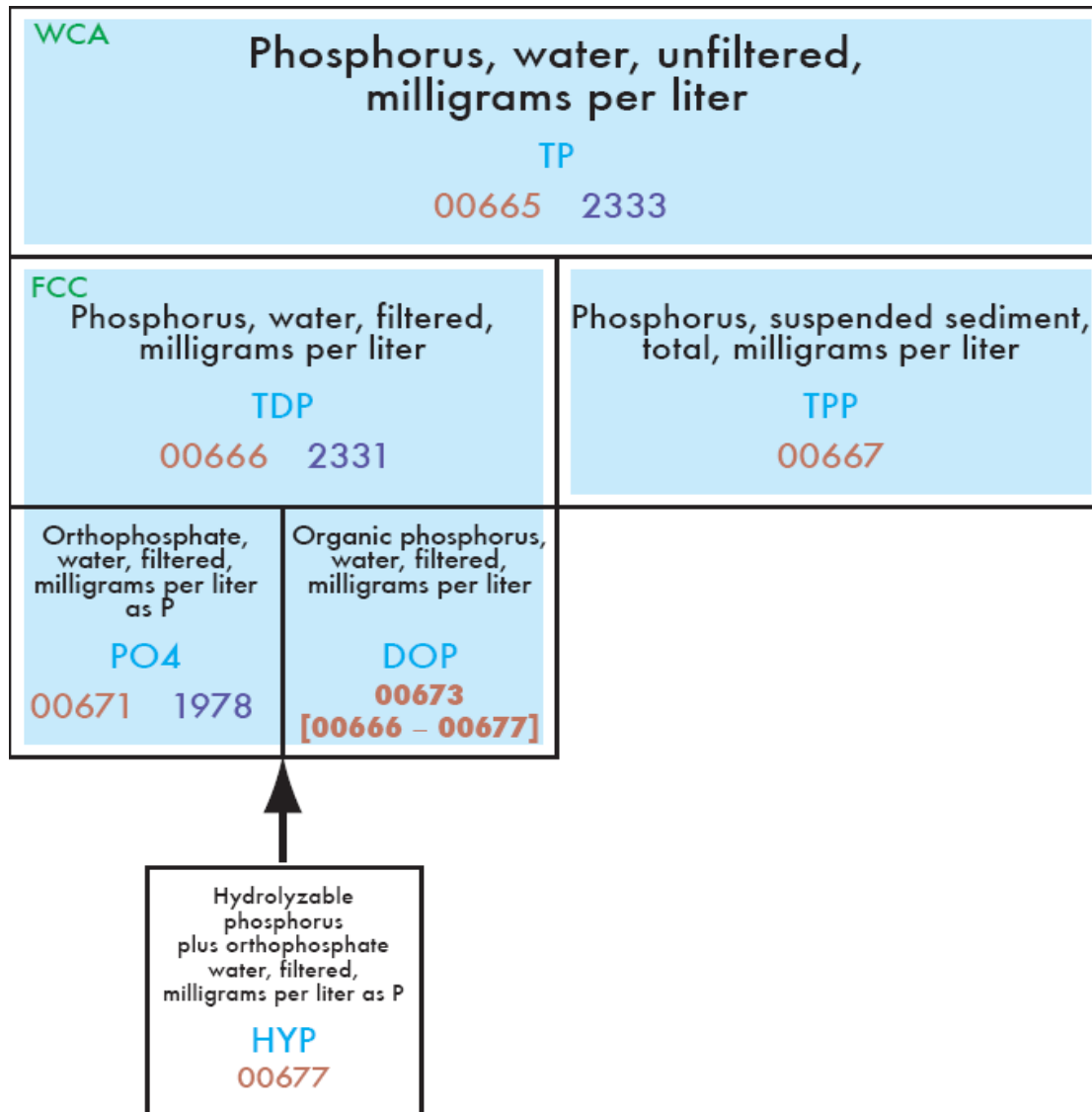
Figure 1: Nitrogen parameters collected for the Maryland RIM Program

<p>Total nitrogen, water, unfiltered, milligrams per liter</p> <p>TN</p> <p>00600 [00625 + 00631] (through 2003) 00600 [62854 + 49570] (2004 and on)</p>			
<p>FCC Total nitrogen, water, filtered, milligrams per liter as nitrogen</p> <p>TDN</p> <p>62854 2754</p>		<p>TPCN* Particulate nitrogen, suspended in water, milligrams per liter</p> <p>TPN</p> <p>49570 2607</p> <p><small>*eff. 11/01/05</small></p>	
<p>Nitrite plus nitrate, water, filtered, mg per liter as N</p> <p>NO23</p> <p>00631 1975</p>	<p>Ammonia, water, filtered, mg per liter as N</p> <p>NH3</p> <p>00608 1976</p>	<p>Organic nitrogen, water, filtered, mg per liter</p> <p>DON</p> <p><small>00607 [00625 - 00608] [through 2003] [TDN, 62854 - 00608 - 00631] (2004 and on)</small></p>	
<p>Nitrite, water, filtered, mg per liter as N</p> <p>NO2</p> <p>00613 1977</p>	<p>Nitrate, water, filtered, mg per liter as N</p> <p>NO3</p> <p>00618 [00631 - 00613]</p>		

Parameter Name

- 62854** Parameter code
- 00618** Parameter code [calculation]
- 2754** Lab code
- TDN** Short name
- **FCC** Bottle (field color indicates sample)

Figure 2: Phosphorus parameters collected for the Maryland RIM Program



Parameter Name

- 00665 Parameter code
- 00673 Parameter code [calculated]
- 2333 Lab code
- TP Short name
- WCA Bottle (field color indicates sample)

Figure 3: Carbon parameters collected for the Maryland RIM Program.

<p>Carbon (inorganic plus organic), water, unfiltered, milligrams per liter</p> <p>TC</p> <p>00690 n/a</p>			
<p>Organic carbon, water, unfiltered, milligrams per liter</p> <p>TOC</p> <p>00680 (through 2003) 114 [TBD, 00681 + 00689]</p>		<p>Inorganic carbon, water, unfiltered, milligrams per liter</p> <p>TIC</p> <p>00685 n/a</p>	
<p>Organic carbon, water, filtered, milligrams per liter</p> <p>DOC</p> <p>00681 2612 DOC (COF)</p>	<p>Organic carbon, suspended sediment, total, milligrams per liter</p> <p>POC</p> <p>00689 [00694 - 00688]</p>	<p>Inorganic carbon, suspended sediment, total, milligrams per liter</p> <p>PIC</p> <p>00688 2608</p>	<p>Inorganic carbon, water, filtered, milligrams per liter</p> <p>DIC</p> <p>00691 n/a</p>
<p>Carbon (inorganic plus organic), suspended sediment, total, milligrams per liter</p> <p>TPC</p> <p>00694 2606</p> <p>TPCN* *eff. 11/01/05</p>			

Parameter Name

- 00681 Parameter code
- 00690 Parameter code [calculation]
- 2612 Lab code
- DOC Short name
- TPCN Bottle (field color indicates sample)

Figure 4: Suspended-sediment parameters collected for the Maryland RIM Program

<p>Sediment Suspended sediment concentration, milligrams per liter</p> <p>SSC</p> <p>80154</p>	
	<p>Suspended sediment, sieve diameter, percent smaller than 0.063 millimeters</p> <p>FIN</p> <p>70331</p>
<p>TSS Residue, total nonfilterable, milligrams per liter</p> <p>TSS</p> <p>00530 169</p>	
<p>Residue, fixed nonfilterable, milligrams per liter</p> <p>MIN</p> <p>00540 [00530 - 00535]</p>	<p>Loss on ignition, from nonfilterable residue, milligrams per liter</p> <p>LOI</p> <p>00535 49</p>

Parameter Name

- 80154 Parameter code
- 00540 Parameter code [calculation]
- 169 Lab code
- SSC Short name
- TSS Bottle (field color indicates sample)

Table 2. Maryland River Input Monitoring Program sampling parameters.
 [NWQL = USGS National Water Quality Laboratory; DHMH = Maryland Department of Health and Mental Hygiene Laboratory]

Lab Code	Parameter Code	Parameter/ Methodology	Reference	Reporting Level
LC 2607 USGS	P49570	Particulate Nitrogen (TPN) <i>Elemental Analysis on filter</i> EPA method 440.0	USEPA (1997)	0.022mg/L
LC 2754 USGS	P62854	Total Dissolved Nitrogen (TDN) <i>Alkaline Persulfate digestion</i> I-2650-03	Patton and others (2003)	0.06 mg/L
LC 1976 USGS	P00608	Dissolved Ammonia (NH₃) <i>Colorimetry, ASF, salicylate-hypochlorite</i> I-2522-90	Fishman (1993)	0.04 mg/L
LC 1977 USGS	P00613	Dissolved Nitrite as Nitrogen (NO₂) <i>Colorimetry, ASF</i> I-2542-89	Fishman (1993)	0.002 mg/L
LC 1975 USGS	PP0631	Dissolved Nitrite & Nitrate as NO₂+NO₃ <i>Colorimetry, ASF, Cd-reduction-diazotization</i> I-2545-90	Fishman (1993)	0.06 mg/L
LC 2333 USGS	P00665	Total Phosphorus (TP) <i>Colorimetry</i> EPA method 365.1	Fishman and Friedman (1989)	0.004 mg/L
LC 2331 USGS	P00666	Total Dissolved Phosphorus (TDP) <i>Acid persulfate (filtered)</i> EPA method 365.1	Am. Public Health Assoc. (1995)	0.004 mg/L
LC 1978 USGS	P00671	Dissolved Orthophosphate (PO₄) <i>Colorimetry, ASF, phosphomolybdate</i> I-2606-89	Fishman (1993)	0.006 mg/L
LC 2612 USGS	P00681	Dissolved Organic Carbon (DOC) UV promoted persulfate oxidation, IR detection O-1120-92	Brenton and Arnett (1993)	0.33 mg/L
LC 2606 USGS	P00694	Total Particulate Carbon (TPC) EPA method 440.0	USEPA (1997)	0.12 mg/L
LC 2608 USGS	P00688	Particulate Inorganic Carbon (PIC) EPA method 440.0	USEPA (1997)	0.12
LC 2611 USGS	P00689	Particulate Organic Carbon (POC) EPA method 440.0	USEPA (1997)	0.12 mg/L
LC 169 USGS	P00530	Total Suspended Solids (TSS) Residue at 105 deg C, gravimetric I-3765-89	Fishman and Friedman (1989)	10 mg/L
LC 49 USGS	P00535	Volatile Suspended Solids (VSS) I-3767-89	Fishman and Friedman (1989)	10 mg/L
n/a	P80154	Total Suspended Sediment (SSC) <i>Filtration, evaporation</i> ASTM test method D3977-97 Method C	Shreve and Downs (2005)	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)	0.2 mg/L
n/a DHMH	P32210	Chlorophyll A (Chlo-a) <i>Hydroscopic glass-fiber filtration</i> EPA 10200	MD DHMH Laboratory	0.1 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 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- μ m (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 with the water-quality samples from the churn splitter or collected separately, 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 analyzed at the Maryland Department of Health and Mental Hygiene (MD DHMH) Laboratory. Samples are placed immediately in the freezer, and within two weeks of collection are either shipped on ice overnight or delivered to the 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.dhmm.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, sediment-transport analysis, quality assurance of sample-collection techniques and field personnel using field blanks and replicates, and accounting for variability within and among the analyzing laboratories. Quality-assurance results can be obtained from: USGS, MD-DE-DC WSC, at 5522 Research Park Drive, Baltimore, Maryland 21228. Laboratory quality-control methods are documented by each laboratory's quality-assurance documents, and are listed above in section B.4 of this report.

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

In past years, the USGS was one of several laboratories participating in a split-sampling program in which samples collected by personnel at the Blue Plains Water Treatment Plant were processed by USGS personnel and submitted to the USGS National Water-Quality-Laboratory in Denver, Colorado. Results were forwarded to MD DNR and USEPA. However, USGS participation in the split-sample program has been limited in recent years.

The USGS did resume participation in this program in WY 2006, and will continue to participate once or twice per year 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 calibrated before each sampling event. Specific instructions for calibration are found in the operating manuals provided with the instrument. Fresh standards are available 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 a logbook and also recorded on the sample field sheet. The logbook serves as documentation for pre- and post-calibration information for each parameter recorded. The log is useful in determining drift in a probe, which indicates that maintenance is necessary for maintenance. 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, 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 project 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://water.usgs.gov>.

Table 3. Maryland River Input Monitoring station 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>				
January 1948 to current year	113	136	6,160	0.35
<u>Susquehanna River at Conowingo (01578310)</u>				
October 1967 to current year	27,000	40,900	1,120,000	269
<u>Patuxent River near Bowie (01594440)</u>				
June 1977 to current year	348	386	8,860	56
<u>Potomac River at Chain Bridge (01646500)</u>				
March 1930 to current year (Values adjusted for diversion)	11,560	11,974	426,000	601

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 (Chlo-A analysis) are sent via hard copy to the RIM data manager, where they are entered into Excel spreadsheets on the USGS computer network. 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 by CD-ROM and raw datasheets. The USGS MD-DE-DC WSC in Baltimore houses the archived copies of the field data sheets and the DHMH data sheets. Copies of the original data sets will be maintained by the project coordinator and provided to MD DNR in hard copy in the form of tables and data summaries. Electronic files with appropriate metadata will be forwarded to the appropriate analysts. The project data manager will maintain field data sheets, which will be stored in fireproof cabinets, per USGS data archive protocols.

Water-quality data are reviewed on a monthly basis. 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 discarded after one month) or the data value verified at the laboratory for transcription errors. Anomalies in the DHMH-analyzed data are noted in the comment field in the Excel spreadsheet. Provisional data files will be transferred from USGS to MD DNR via CD-ROM or file transfer protocol via the Internet as described in section A.5. These intermediate data transfers include streamflow data from each station for the previous water year, provisional water year nutrient and suspended-sediment data and quality-control results, and provisional mean-monthly and annual load estimates for each nutrient and suspended-sediment parameter monitored during the previous water

year. Metadata files created by the data manager and linked to the data files also will be transferred to MD DNR. A final WY 2008 water-quality concentration data set, and revised (considered final) water year 2004, and interim WY 2005-2008 mean-monthly and annual nutrient and sediment loads will be forwarded on CD-ROM to J. Shermer Garrison by June 30, 2009.

B.11 Data Analysis

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

Although a simple linear model can adequately describe a streamflow-parameter concentration relation for some nutrient or suspended-sediment constituents, such a model will not work for all constituents. A single model that can simulate the variable streamflow-concentration relations in different watersheds and other issues would be helpful. Past experience has shown that the quadratic flow parameter was significant for many monitored constituents, which indicates that the relation of concentration to water discharge for these constituents requires a more complex model. For some constituents, seasonal variability in concentration occurs, and a single model should be able to account for seasonality. Finally, a sufficiently long record can help determine trends or changes in concentration over time, but when a data record is long enough, changes in trends (acceleration or deceleration in trend) may occur for some constituents, and a model needs to be able to determine changes in trends.

Load-Estimation Procedure

Load estimates were calculated using multi-variate linear regression. Monthly and annual mean-daily loads were calculated for each river for total nitrogen (TN), dissolved nitrite plus nitrate (NO₂+ NO₃), total phosphorus (TP), dissolved ortho-phosphorus (PO₄), and total suspended sediment (SSC).

Estimates of constituent loading provide critical information on the amount and timing of material reaching downstream water bodies. A load is an integrated mass flux over some time interval $\{t_a, t_b\}$:

$$L = \int_{t_a}^{t_b} l(t)dt = \int_{t_a}^{t_b} kc(t)q(t)dt$$

where

- L is the total load;
- l is the instantaneous load;
- k is a unit conversion factor;
- c is the instantaneous observed concentration; and
- q is the instantaneous streamflow.

The load represents the amount of a given constituent transported and delivered downstream of the point at which measurements of c and q are made q .

The USGS log-linear regression model (ESTIMATOR) developed by Cohn and others (1989) is used by the USGS's River Input Monitoring Program to estimate loads of nutrients and suspended sediment. The program computes loads in two steps. First, a center-estimate linear model is fit to the logarithms of the concentration. The model uses the Minimum Variance Unbiased Estimator (MVUE) developed by Bradu and Mundlak (1970) to correct for retransformation bias arising when model results using the logarithm of c are transformed into "real" units. The Adjusted Maximum Likelihood Estimator (AMLE) (Cohn, 1988) is used to assign concentration values to censored data, which are data reported as less than the analytical reporting limit. USGS will document the results and standard procedures used to estimate loads for total nitrogen. Coefficients estimated using AMLE are nearly-unbiased, and the variance of the sums of loads is easy to compute. AMLE is identical to ordinary least squares for the case where no observations are censored. A 7-parameter model is used to estimate loads for the RIM Program sites:

$$\ln(c) = \hat{\beta}_0 + \hat{\beta}_1 \ln(q/q_c) + \hat{\beta}_2 [\ln(q/q_c)]^2 + \hat{\beta}_3 (t - t_c) + \hat{\beta}_4 (t - t_c)^2 + \hat{\beta}_5 \sin(2\pi t) + \hat{\beta}_6 \cos(2\pi t) + \varepsilon \quad (1)$$

where

- \ln is the natural logarithm function;
- c is measured concentration, in milligrams per liter;
- q is measured daily-mean streamflow, in cubic feet per second;
- t is time, in decimal years;
- q_c, t_c are centering variables for streamflow and time;
- $\hat{\beta}_i$ are coefficients estimated by ordinary least squares (non-censored observations) and AMLE (censored observations);
 - $\hat{\beta}_0$ is a constant;
 - $\hat{\beta}_1, \hat{\beta}_2$ describes the relation between concentration and streamflow;
 - $\hat{\beta}_3, \hat{\beta}_4$ describe the relation between concentration and time, independent of flow;
 - $\hat{\beta}_5, \hat{\beta}_6$ describe seasonal variation in concentration data; and
- ε is residual error, assumed to be normally distributed with zero mean and variance σ_ε^2 .

Centering variables are defined such that time and time-squared (and flow and flow-squared) predictor variables are orthogonal (independent). Centering of variables simplifies numerical calculations but has no effect on load estimation. The model defined in this way has flow and time terms as independent predictors. Because estimates are conditioned on flow, the model automatically accounts for any bias in the sampling strategy. A sampling protocol that targets high- and low-flow conditions reduces the error in load estimates generated by the model due to the log-linear relationship between concentration and flow.

After the model coefficients have been estimated, daily concentrations are computed. Daily concentrations are then used to estimate daily loads (and variances) using daily-mean streamflow. Daily loads are summed to produce monthly and annual loads. The standard errors are estimated using formulas in Gilroy and others (1990) and Cohn and others (1992).

For the nine RIM Program sites, loads are estimated using model described above and method described in the USGS Water-Resources Investigations Report (WRIR) 00-4156 (Yochum, 2000). The revised method estimates loads using the fifth, or center, year of a sliding 9-year window. Each year a new model is run for each station and constituent, the most recent year is added, and the previous four years of estimates are updated. Model results and regression summaries will be used to characterize the relation of constituent concentration to river discharge and season, and to determine long-term trends in constituent concentration. Loads are reported annually to USGS cooperators and the public through the RIM web site located at the following address:
[http:// va.water.usgs.gov/chesbay/RIMP/index.html](http://va.water.usgs.gov/chesbay/RIMP/index.html).

The load-estimation procedure described above is desirable for several reasons. The model is sufficiently flexible to capture many of the characteristics of real constituent data; it is easy to use--ordinary least squares is a particularly easy method for fitting data; statistical properties of the estimates are well understood; it employs only seven parameters to describe discharge, seasonality, and time trends; and it has generally been found to "explain" between 10 and 80 percent of the variability observed in the logarithms of constituent concentration data.

Calibration Data

For each year, the load-estimation model is calibrated using the data set collected and analyzed by the USGS from that site for the previous 9 years. For the Susquehanna, Potomac, Patuxent, and Choptank Rivers, a constant 9-year window is used, with the middle year considered the best and "final" load estimate and the final four loading years considered "provisional".

Seasonal Variability and Long-Term Trends in Constituent Concentration Data

Model results and regression summaries are used to characterize the relation of constituent concentration to river discharge and season, and to determine if concentration has changed over time. Model results and regression summaries are documented and parameter coefficients ($\hat{\beta}_i$) are tabulated for each constituent. Statistically significant parameters are identified; a (+) sign indicates positive parameter coefficients and a (-) sign indicates negative parameter coefficients. Regression statistics, R^2 (standard error) are determined and included in the summaries.

Interpretations of model results are based on the significance and sign (+/-) of model parameters. Model parameters are considered significant if the regression statistic p-value is greater than 0.05 and the absolute value of the t-statistic is greater than 2.0. Significance of the model parameter indicates a relation between constituent concentration and the corresponding model variable (discharge, time, or season). The sign of a model parameter indicates whether it has a positive (+) relation to the concentration or a negative (-) relation.

The relation between constituent concentration and discharge is defined in the model form by both a linear ($\ln(q/q_c)$) and a quadratic-flow variable ($[\ln(q/q_c)]^2$). A significant linear parameter indicates a linear relation between concentration and discharge. A significant quadratic parameter indicates a non-linear relation between concentration and discharge. If both the linear and quadratic-flow parameters were significant, an acceleration (+) or deceleration (-) in constituent concentration occurred. For example, a significant positive linear-flow parameter combined with a significant negative quadratic-flow parameter indicated that concentration would increase with increasing flow, but the rate of increase in concentration would decelerate, or decline, at higher flows.

The relation between constituent concentration and time is represented by both a linear ($t - t_c$) and quadratic-term variable ($(t - t_c)^2$) in the model form. A significant linear parameter indicates an upward (+) or downward (-) linear trend in constituent concentration. A significant quadratic parameter indicates a non-linear relation between concentration and time. For example, a significant, positive quadratic parameter indicates a decreasing trend in early years followed by an increasing trend in later years. A significant, negative quadratic parameter indicates the opposite. If both the linear and quadratic-time trend parameters were significant, then an acceleration (+) or deceleration (-) in trend occurred in later years.

Seasonality was defined in the model form by two variables, $\sin(2\pi t)$ and $\cos(2\pi t)$. If one or both of the seasonality variables were significant, seasonality was considered an important factor in describing the variability in constituent concentration at the four river stations.

Estimates of Loads

The same model form (1) is used to estimate monthly and annual mean-daily loads for each constituent at each of the monitoring stations. Although all parameters are included in each of the model runs, not all parameters are significant. The presence or absence of a non-significant parameter does not affect the value of the resulting load estimate. However, inclusion of non-significant parameters does result in slightly larger standard errors of the estimate, which causes an over-estimation of confidence limits for the estimates. As this results in a slight understatement of the accuracy of the estimates, using all seven parameters in the model provides for a conservative assumption.

Residuals are reviewed for determining whether serious violations of the assumption of normality occur and that all of the models reasonably represent the data. The statistical significance of each model equation is determined.

Monthly and annual mean-daily load estimates for the following constituents are calculated for the River Input sites: TN, NO₂+NO₃, TP, PO₄, and SSC. Error terms also are calculated. Monthly load estimates can be calculated by multiplying the mean-daily load by the number of days in a given month. Annual loads can be calculated by multiplying the mean-daily load by 365 days.

It is understood that the relation between concentration and streamflow may change over time due to changes in land use, wastewater discharges, best management practices and climate change, so a moving window approach was developed to estimate loads. For some parameters in the four Maryland rivers, differences were observed for loads estimated using a 14-year (1985-1998) and a 10-year (1989-1998) model window, especially those near the tail of the calibration period. Estimates near the center of a model window (Year-5 of a desired 9-year window) have the least uncertainty. Load estimates in the first and last 4-year period are considered preliminary and are revised each year. So, for each year, a new model is run for each site and constituent, the most recent year of data are added to the data set and the previous 4 years of estimates are updated. The fifth (middle) year of data is considered to be the best estimate and is kept in the final database. This revised methodology provides a greater confidence in load estimation (Yochum, 2000).

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 principal investigator will be immediately notified of any deficiencies and take immediate corrective actions.

The project coordinator will continually monitor the logs and records associated with the project to assure that project schedules are being met. The project coordinator 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 will be 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 Manager (USGS) will be 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 on a monthly basis. 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 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 data 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. Summary information is provided in charts and tables. A data analysis log is maintained which documents steps taken in data reduction and statistical printouts and results of any analyses performed.

D.2 Validation and Verification Methods

The field technician or senior field staff person will verify all data entered on the field data sheet. This person will examine all data sheets to ensure that they are accurately and legibly completed. They will then sign and record the date and time on the data sheets when verified. All field validation must occur prior to leaving the site before samples are discarded. Any recording errors are to be marked through and initialed. The true value is to be recorded next to the error, and all errors are to be explained in the remarks column of the data sheet.

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 QA officer assures that samples are collected, labeled and preserved in accordance with standard operating procedures. Field blanks and trip 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 are computed by ESTIMATOR 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.). ESTIMATOR output includes regression diagnostics (Draper and Smith, 1998) section. Visual examination of the output plots, reviewing of errors of prediction, and testing for normality by using the probability plot correlation coefficient (PPCC) test are done on each individual model. The USGS Project Manager is responsible for performing quality control through a technical review by colleague and associate USGS staff inside and outside the River Input project.

E. References

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Attachment A: USGS Water-Quality Field Data Sheet



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. SIF 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): EWM [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 B: USGS NWQL Schedule 1965 for Nutrient Analysis

NWQL Catalog

Schedule 1965

[Add To Favorites](#)

Description: Chesapeake Bay River Inputs Project

Price: \$239.36

Owner: MD

Analyzing Laboratory(s):

USGS - National Water Quality Laboratory, Denver, CO

Analyte	Lab Code	Parameter Code	M	CAS Number	RL	Unit	RL Type	Container
Inorganic carbon	2608	00688	B		0.12	mg/L	mrl	TPCN
Total carbon	2606	00694	A		0.12	mg/L	mrl	TPCN
Organic carbon	2611	00689	B		0.12	mg/L	mrl	TPCN
Organic carbon	2612	00681	D		0.33	mg/L	lrl	DOC
nitrogen, ammonia	1976	00608	F	7664-41-7	0.04	mg/L	lrl	FCC
nitrogen, nitrite	1977	00613	H	14797-65-0	0.004	mg/L	lrl	FCC
nitrogen, nitrite + nitrate	1975	00631	E		0.060	mg/L	lrl	FCC
Total nitrogen	2607	49570	A	17778-88-0	0.022	mg/L	mrl	TPCN
Total nitrogen (NH3+NO2+NO3+Organic), filtered	2754	62854	A	17778-88-0	0.06	mg/L	lrl	FCC
Phosphorus	2331	00666	G	7723-14-0	0.004	mg/L	lrl	FCC
phosphorus, phosphate, ortho	1978	00671	I	14265-44-2	0.006	mg/L	lrl	FCC
Phosphorus	2333	00665	G	7723-14-0	.004	mg/L	lrl	WCA
residue	169	00530	B		10	mg/L	mrl	SUSO
residue, volatile	49	00535	A		10	mg/L	mrl	SUSO
Silica	56	00955	C	7631-86-9	0.20	mg/L	lrl	FU

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

Container Requirements

Quantity	Bottle
1	100mL DOC Description: 125 mL Glass bottle, amber Treatment and Preservation: Bottle baked at 450 deg C by laboratory. DO NOT RINSE BOTTLE BUT RINSE FILTER WITH ORGANIC-FREE WATER. Filter sample using supor or glass fiber filter (see Lab Code description above for filter type) , acidify to pH < 2 with 1 mL of 4.5N sulfuric acid (H2SO4), chill and maintain at 4 deg C, ship immediately. Glass fiber filter may be retained for Total Particulate Carbon or Particulate Inorganic Carbon analysis.
1	125mL FCC Description: 125 mL Brown polyethylene bottle, Treatment and Preservation: Filter through 0.45-um filter, use filtered sample to rinse containers, chill and maintain at 4 deg C, ship immediately
1	25mL FU Description: 250 or 500 mL Polyethylene bottle, Treatment and Preservation: Filter through 0.45-um filter. Use filtered sample to rinse containers
1	250mL SUSO Description: 250 or 500 mL Polyethylene bottle, Use unfiltered sample to rinse bottles Treatment and Preservation: dedicated bottle for lab code 169
1	1Filter TPCN Description: Treatment and Preservation: Filter sample with 25 mm glass fiber filter. Fold filter in half and place in aluminum foil pouch. Send 3 filters. Place the pouch in Whirlpak bag. Chill to 4 deg C. ship immediately. Provide volume of sample passed through filter in comments to NWQL place on the

ASR.

125mL [WCA](#)

- 1 **Description:** 125 mL Plain (translucent) polyethylene bottle, Use unfiltered sample to rinse bottles
Treatment and Preservation: acidify with 1 mL of 4.5N (4.5 normal) sulfuric acid (H₂SO₄), chill and maintain at 4 deg C, ship immediately.

References

1. **EPA 365.1**
Determination of Phosphorus by Semi-Automated Colorimetry Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples
2. **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
3. **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-1120-92
4. **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-2522-90 , I-2542-89 , I-2545-90 , I-2606-89
5. **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-2700-89 , I-3765-89 , I-3767-89
6. [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
7. [OWQ Tech Memo 2000.08](#)
New Method for Particulate Carbon and Particulate Nitrogen, June 1, 2000
8. [OWQ Tech Memo 2000.08](#)
New Method for Particulate Carbon and Particulate Nitrogen, June 1, 2000
9. [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
10. [Memo -- USEPA Approval for nationwide use of ATP method](#)
Telliard, W.A., USEPA, Director of Analytical Methods, Engineering and Analysis Division

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	M D User Code	2 4 2 7 B 4 8 0 1 Project Account	LAB USE ONLY NWQL LABORATORY ID
0 1 5 7 8 3 1 0 STATION ID	2 0 0 7 Begin Date (YYYYMMDD)	Begin Time	9 9 Medium Code Sample Type
Brenda Majedi (410) 238-4227 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: _____	Lab Code: _____	Lab Code: _____	Lab Code: _____
Lab Code: _____	Lab Code: _____	Lab Code: _____	Lab Code: _____	Lab Code: _____ A D
Lab Code: _____	Lab Code: _____	Lab Code: _____	Lab Code: _____	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		

**Attachment D: Example of Quarterly Report to Maryland Department of
Natural Resources**

EXAMPLE

Chesapeake Bay River Input Monitoring Program

Quarterly Progress Report

January 1, 2006 – March 31, 2006

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)

Funding: Maryland DNR and USGS

Internal Acct #s: 2427-B4800, B4801

Start Date: July 1985

Completion Date: Ongoing

Project Personnel:

Jeff Raffensperger, Hydrologist

Brenda Majedi, Hydrologic Technician

Dave Brower, Hydrologic Technician

Project Objectives:

- Determine the ambient concentration of nutrient and suspended sediment water-quality samples 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.

Activities This Quarter:

- Ongoing sampling program.

EXAMPLE

Sampling Summary:

Site	Sample Type		
	Routine	Storm	QA/QC
Susquehanna @ Conowingo	3	2	1
Potomac @ Chain Bridge	3	2	1
Patuxent nr. Bowie	3	2	1
Choptank nr. Greensboro	3	2	1

Plans for Next Quarter:

- Collect 1 routine sample (fixed-interval frequency) per month at all four sites.
- Collect monthly storm flow samples at each site, depending on hydrologic conditions.
- Complete quarterly progress report to be submitted to Maryland DNR.