

Scope of Work

Discrete and Continuous Water-Quality Monitoring for Nutrients, Sediment, Metals, Bacteria, and Organics, Anacostia Watershed, Maryland

- **A Cooperative Project between the U.S. Geological Survey (USGS),
Prince George's County (PGC),
Maryland Department of the Environment (MDE),
and the U.S. Environmental Protection Agency (EPA)**

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*A Cooperative Project between the U.S. Geological Survey (USGS), Prince
George's County (PGC), Maryland Department of the Environment
(MDE), and the U.S. Environmental Protection Agency (EPA)*

Summary

Problem. The Anacostia watershed is one of the most densely populated watersheds within the Chesapeake Bay drainage basin and has undergone many changes through the years, mainly due to the influence of urbanization on the ecosystem. The broad goal of the proposed study described herein is to significantly expand data collection to include water-quality sampling and analysis for a wide suite of natural and anthropogenic constituents.

Objectives. The USGS has responsibility for the following objectives: 1) install housing and equipment for water-quality sample collection at two Anacostia River USGS stream gage sites in Prince George's County (01649500, NORTH EAST BRANCH ANACOSTIA RIVER AT RIVERDALE, MD; 01651000 NW BRANCH ANACOSTIA RIVER NEAR HYATTSVILLE, MD); 2) install equipment to provide real-time reporting of additional water-quality parameters (pH, temperature, specific conductance, turbidity); develop regression relations to estimate continuous nitrate (NO₃), total nitrogen, total phosphorus, bacteria (*E. coli*), and suspended-sediment concentrations (when possible); and 3) collect and analyze monthly and storm samples at the two sites for a suite of constituents; manage all data collection and quality assurance/quality control efforts; manage all data and publish annually in the MD-DE-DC District data report (excluding organics data, to be managed and reported by George Mason University).

Benefits and relevance. Data collected as described in this proposal, combined with existing data from other USGS studies and historical and ongoing monitoring by other county, state, and federal agencies, will provide valuable information for future management of the Watershed. The study described in this proposal meets several goals of the Water Resources Division (WRD) of the USGS, by: 1) providing data or results useful to multiple parties in potentially contentious inter-jurisdictional conflicts over water resources; 2) providing water-resources information that will be used by multiple parties for planning and operational purposes; and 3) contributing data to national databases that will be used to advance the understanding of regional and temporal variations in hydrological conditions.

Approach and methods. Automatic samplers will be installed at all feasible sites to collect storm samples; regular baseflow and high-flow samples will also be collected. All samples will be collected using USGS protocols and analyzed for nutrients and trace metals at the National Water-Quality Laboratory (NWQL) in Denver; suspended-sediment analyses will be done at the USGS Kentucky Sediment Laboratory; bacteriological analyses will be performed at the Maryland Department of Health and Mental Hygiene Laboratory (DHMH); and organics will be analyzed at the Department of Chemistry Laboratory, George Mason University (GMU).

Project timeline. The project began on April 1, 2003. Discrete water-quality data collection began in July 2003 and is scheduled to end on June 30, 2006, which will provide a maximum of 36 months of water-quality monitoring data, depending on the constituent. The project period will extend through September 30, 2007, to allow time for data interpretation and completion of an interpretive report.

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Problem

The Anacostia Watershed encompasses 456 km² (176 mi²) within suburban Maryland and the District of Columbia, and crosses two major physiographic provinces, the Coastal Plain and Piedmont (Figure 1). The Anacostia watershed is one of the most densely populated watersheds within the Chesapeake Bay drainage basin (Figure 2). The Watershed has undergone many changes through the years, mainly due to the influence of urbanization on the ecosystem. Major restoration efforts began in 1987.

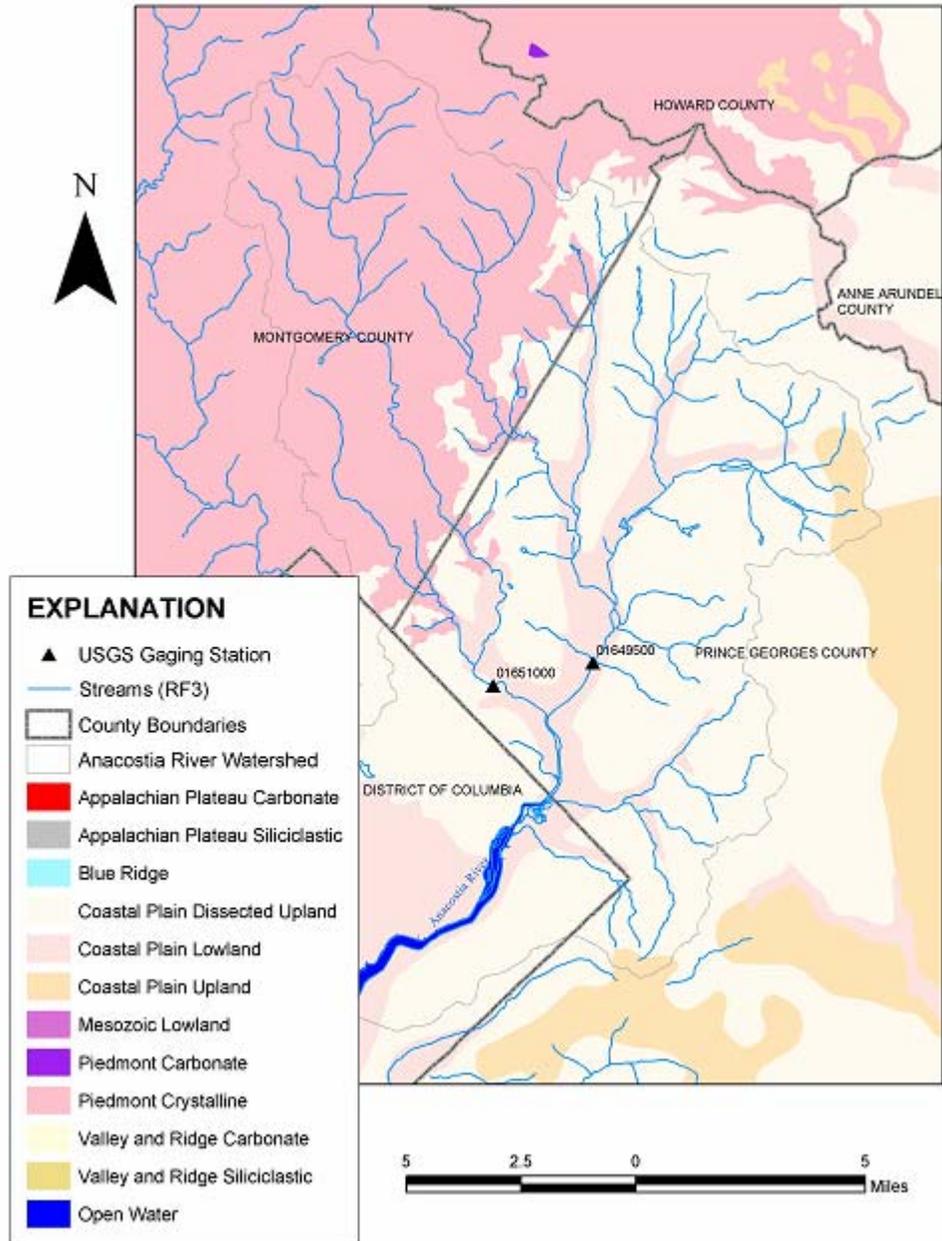


Figure 1. Physiographic features of the Anacostia Watershed.

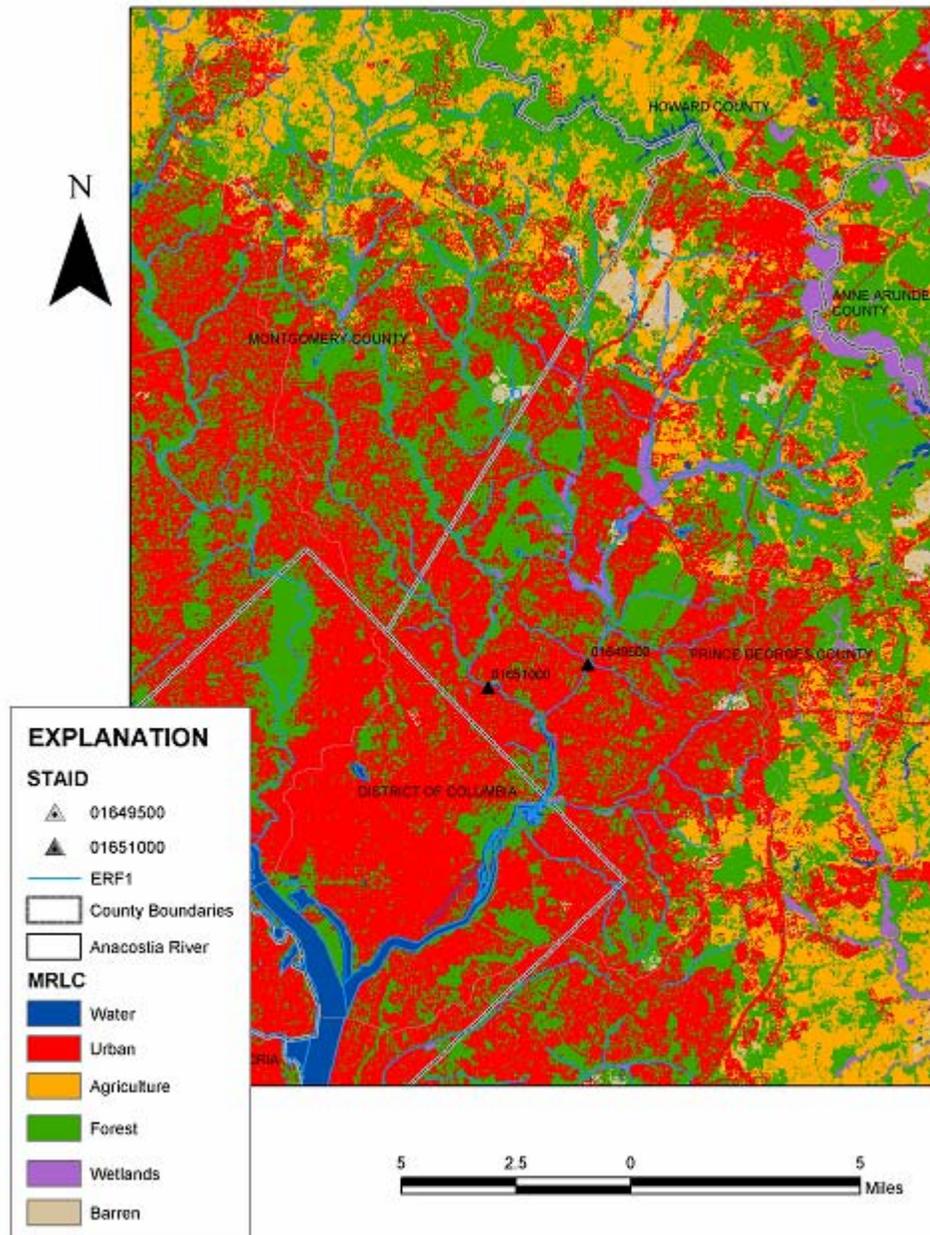


Figure 2. Land use in the Anacostia Watershed.

An estimated 90% of the original wetlands in the Watershed have been lost. The Watershed has been designated one of only three of the region's Areas of Concern by the Chesapeake Bay Program due to risk to aquatic life. A fish consumption ban was imposed by the District of Columbia due to PCB and pesticide contamination of fish. Loss of habitat, erosion, sedimentation, flooding, destruction of wetlands, channelization, toxic pollution, decaying older communities and waterfront areas and loss of river-based recreational opportunities such as boating, fishing and swimming all characterize what had become of the Anacostia River and much of its watershed.

A landmark agreement was reached between Maryland and the District of Columbia in 1984 that officially recognized the need for restoration. A 1987 agreement added Montgomery and

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Prince George's Counties into the restoration partnership. In 1991, this partnership adopted, through its "Six-Point Action Plan," six broad-sweeping goals designed to restore the Anacostia River and its tributaries (<http://www.anacostia.net/agreement.htm>). The Anacostia Watershed Toxics Alliance (AWTA) was formed in March 1999 under the premise that a voluntary partnership, focused on the task of addressing toxic sediment contamination of the tidal Anacostia, would offer a more efficient and appropriate alternative to address contamination issues.

USGS currently maintains two stream gages (station IDs 01649500 and 01651000) on the Northeast and Northwest branches (Figure 1), in cooperation with Prince George's County and the Metropolitan Washington Council of Governments (MWCOG). The broad goal of the proposed study described herein is to significantly expand data collection to include water-quality sampling and analysis for a wide suite of natural and anthropogenic constituents (nutrients, sediment, metals, bacteria, and organics such as PCBs and PAHs).

Objectives

The USGS has responsibility for the following objectives:

OBJECTIVE 1. Install housing and equipment for water-quality sample collection at two Anacostia River USGS stream gage sites in Prince George's County (01649500, NORTH EAST BRANCH ANACOSTIA RIVER AT RIVERDALE, MD; 01651000 NW BRANCH ANACOSTIA RIVER NEAR HYATTSVILLE, MD).

OBJECTIVE 2. Install equipment to provide real-time reporting of additional water-quality parameters (pH, temperature, specific conductance, turbidity). In 2006 (project year 3), once sufficient samples have been collected and analyzed, begin developing regression relations to estimate (when possible) continuous nitrate (NO₃), total nitrogen, total phosphorus, bacteria (*E. coli*), and suspended-sediment concentrations. Regression relations will be completed and published in an interpretive report in 2007 (project year 4).

OBJECTIVE 3. Collect and analyze monthly and storm samples at the two sites for a suite of constituents, following methods and sampling plans described below; manage all data collection and quality assurance/quality control efforts; manage all data and publish annually in the MD-DE-DC District data report (excluding organics data, to be managed and reported by George Mason University).

Benefits and Relevance

Participants in the Anacostia Watershed Toxics Alliance (AWTA) need tools and data to evaluate alternative approaches for correcting existing water-quality and water-quantity problems, and for forecasting future conditions within the Anacostia Watershed. Data collected as described in this proposal, combined with existing data from other USGS studies and historical and ongoing monitoring by other county, state, and federal agencies, will provide valuable information for future management of the Watershed. Specifically, these data will provide baseline concentrations and loads for a large number of chemical contaminants in the Anacostia River and sediments.

The study described in this proposal meets several goals of the Water Resources Division (WRD) of the USGS, by: 1) providing data or results useful to multiple parties in potentially contentious inter-jurisdictional conflicts over water resources; 2) providing water-resources information that will be used by multiple parties for planning and operational purposes; and 3) contributing data to national databases that will be used to advance the understanding of regional and temporal variations in hydrological conditions.

Study Area and Background

The Anacostia Watershed exhibits ecological and physical diversity. The Watershed extends into two physiographic provinces and three political jurisdictions (Figure 1). There are three major drainage areas comprising the Anacostia Watershed: the Northwest Branch, the Northeast Branch, and the tidal drainage (Figure 3). The Northwest and Northeast branches are free-flowing (non-tidal) streams, and their confluence forms the tidal Anacostia River in the vicinity of Bladensburg, Maryland. The tidal drainage area consists of the tidal river and its floodplain, as well as small Coastal Plain streams that flow directly to the tidal river; most of these streams are enclosed in storm sewer systems. The tidal reach of the Anacostia River is 13.5 kilometers (8.4 miles) in length from the confluence of the Northwest and Northeast branches downstream to the Potomac River. The river joins the Potomac approximately 174 kilometers (108 miles) upstream of Chesapeake Bay.

From the time of the first European settlement to the Civil War, the forested Watershed was progressively cleared for agriculture. Tobacco, corn and cotton farming dominated the land use in the Watershed. Most of the watershed was reportedly brought under cultivation by 1860. This initial wave of change led to increasing sedimentation of the Anacostia River. Soil eroding from upland agricultural fields was transported downstream to the tidal river, rendering the thriving port of Bladensburg useless by 1850. This accelerated sedimentation continued through the latter half of the century, resulting in the formation of extensive mud flats along the banks of the tidal river. In 1902, Congress approved funding for the U.S. Army Corps of Engineers to dredge portions of the tidal Anacostia up to the Anacostia Navy Yard, as well as a smaller channel upstream to the District line.

Since the late nineteenth century, ecological problems in the Anacostia Watershed have largely resulted from an expanding human population and the associated changes in land use and land cover. The ongoing loss of forest and wetland habitat, alteration of streamflow, increases in nonpoint source pollution, and discharges of combined sewer overflow and industrial waste have all contributed to the decline in the ecological health of the watershed. These shifts in land use patterns over the last three centuries have drastically changed the ecology of the watershed.

As noted in the AWTA Statement of Purpose from December 19, 1999 (<http://response.restoration.noaa.gov/cpr/watershed/anacostia/guide/home/awtasop.html>), historically, many industries were based along the banks of the Anacostia River. Over the years, hazardous substances from these industries and other human activities were discharged directly into the river or were washed into the river by runoff. The Watershed also has experienced substantial deforestation and agricultural development, intense and continuous urbanization, industrial development, and significant loss of fringe wetlands and marshes. The River has been severely stressed by the effects of point and non-point source discharges of contaminants brought about by these changes within the Watershed.

This has resulted in significant sedimentation and elevated levels of hazardous substances, including polychlorinated biphenyls (PCBs), pesticides such as chlordane, lead and other heavy metals, and polynucleararomatic hydrocarbons (PAHs) in sediment throughout the 13.5-kilometer run of the Anacostia River. In addition, the lower reach of the River within the District of Columbia is subject to raw sewage discharges from Combined Sewer Overflows (CSO) during rain events exceeding one-half inch. Significant sedimentation during wet weather flows also impacts and deteriorates the river morphology.

Some of these hazardous substances have been found in fish at levels that endanger the health of the fish. Numerous fish in the river exhibit tumors and lesions. In addition, hazardous substances have been found in the fish at levels that may threaten the health of people who eat them. The District of Columbia declared several fish consumption health advisories in the 1990s with restrictions on bottom-feeding species and game fish, and a fish consumption ban for pregnant women and children.

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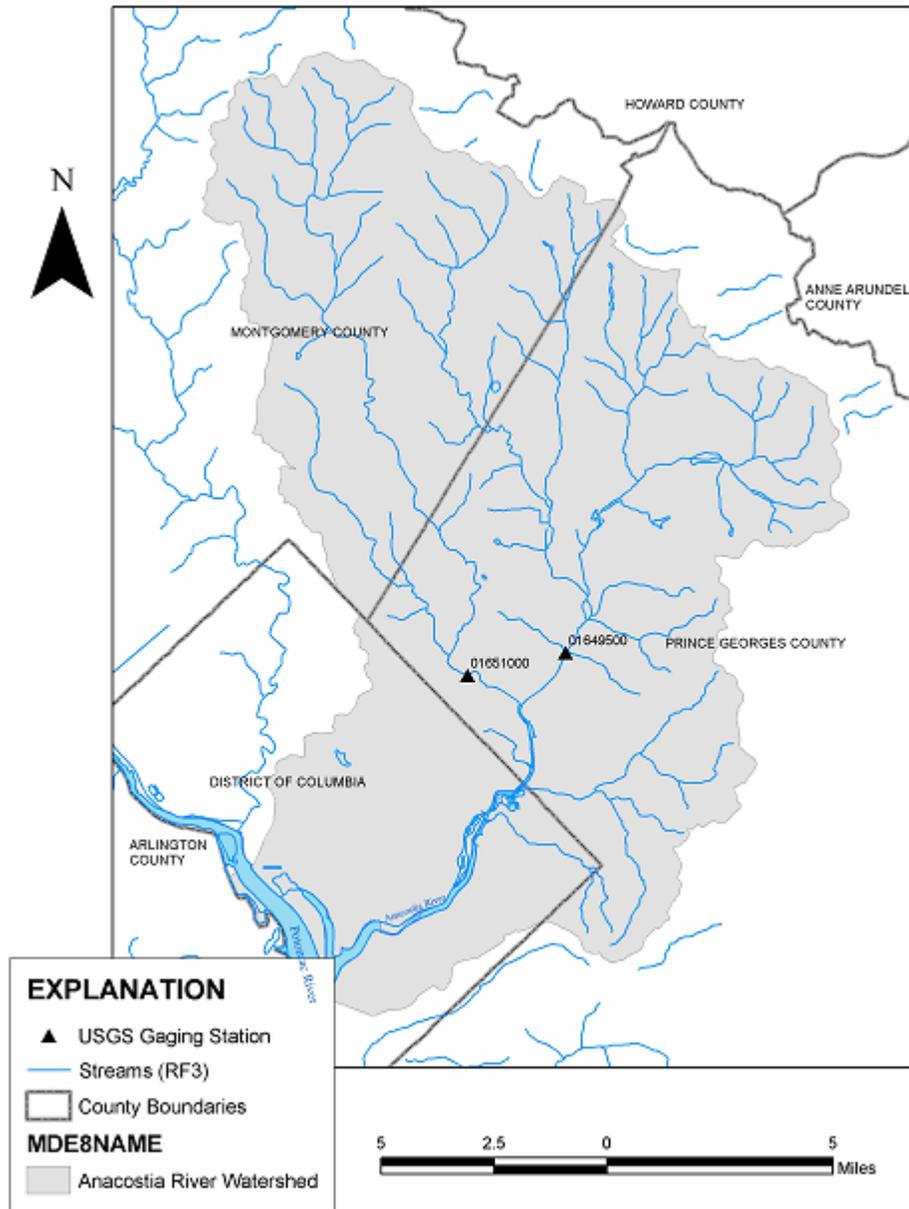


Figure 3. Hydrographic features of the Anacostia Watershed.

Methods and Approach

Water-Quality Sampling and Analysis

Samples for water-quality analysis will be collected using both manual field-sampling methods following USGS protocols (U.S. Geological Survey, 1997 to present), and automatic samplers. Two refrigerated automatic samplers will be located at each site, and will be used primarily to collect stormflow samples. The sampler used for inorganic analyses (nutrients, trace metals, suspended sediment, TSS, BOD) will be stocked with 24 precleaned 1-L fluorinated polyethylene bottles. The sampler will be programmed to collect six discrete samples (four 1-L bottles per sample) at fixed time intervals over the rise, peak, and fall of the hydrograph. The sampler used for the organics analyses by GMU will be stocked with one precleaned 20-L glass bottle, and the sampler will be programmed to collect a composite sample comprised of six ~3.3-L samples collected at fixed time intervals over the rise, peak, and fall of the hydrograph. Both samplers will be equipped with a pressure transducer to measure fluid pressure (stage), a precipitation gage, and a data logger. Sample collection may be initiated by predetermined precipitation intensity or by a rise in stream stage above a specified value and will proceed at timed intervals. Sampling will proceed throughout the event, although not all samples may be analyzed for any given storm. Rather, samples will be selected for analysis on the basis of their timing relative to the rise, peak, and recession of the storm hydrograph. Samples will be collected over varying seasons and streamflow conditions in order to capture hydrologic variability.

All samples will be analyzed at: the USGS National Water-Quality Laboratory (NWQL), in Denver, Colorado, for nutrients, trace metals, total organic carbon (TOC), and total suspended solids (TSS); the USGS Kentucky Sediment Laboratory, for suspended sediment; at the Department of Chemistry Laboratory, George Mason University, for organics; and the Maryland Department of Health and Mental Hygiene Laboratory (DHMH) for biological oxygen demand (BOD) and bacteriological analyses.

USGS Watstore Code	Constituent	Reporting Limit
00010	Water Temperature (°Celsius)	0.5
00300	Dissolved Oxygen (mg/L)	0.5
00095	Specific Conductance (µS/cm)	0.1
00400	pH	0.1
63680	Turbidity (FNU)	0.1
00680	TOC (mg/L)	0.4
00310	BOD (mg/L), 5-day	2.0
00666	Soluble Phosphorus (mg/L as P)	0.004
00625	Total Kjeldahl Nitrogen (mg/L as N)	0.10
00665	Total Phosphorus (mg/L as P)	0.004
00623	Soluble Kjeldahl Nitrogen (mg/L as N)	0.10
00671	Orthophosphate (mg/L as P)	0.006
00613	Nitrite (mg/L as N)	0.002
00631	Nitrite + Nitrate (mg/L as N)	0.016
00608	Ammonium (mg/L as N)	0.010

Table 1. Reporting limits for field parameters, TOC, BOD, and NWQL schedule 1119 for nutrients.

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Sampling and analytical methods for nutrients, TOC, BOD

Nutrient samples will be collected using USGS sampling techniques and composited in a polyethylene churn splitter. Samples for whole-water analysis are collected directly from the churn and 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 polycarbonate capsule filter. Samples are shipped on ice overnight to the NWQL in Denver, Colorado, and are analyzed within 5 days of arrival. Nitrogen and phosphorus are analyzed by colorimetric methods using air-segmented continuous-flow analyzers (Alpkem Corp., Clackamas, Ore.), operated with pecked sampling and bubble-gated detectors (Patton and Wade, 1997). Kjeldahl nitrogen and phosphorus (Watstore codes 00666, 00625, 00625, and 00671) are predigested batch-wise using a Tecator Digestion System 40, model 1016 block digester (Patton and Truitt, 1992). USGS reporting limits are listed in Table 1 (Fishman, 1993; Patton and Truitt, 1992). All NWQL laboratory methods are documented and verified for bias, accuracy, and precision with standard reference materials and participation in the USGS Office of Water Quality sample-testing program (Maloney, Ludtke, and Krizman, 1994; Pritt and Raese, 1995). Field blanks, equipment blanks, and field duplicates and comparison samples are also collected to monitor bias and precision in all aspects of data collection.

Samples for Total Organic Carbon (TOC) analysis will be collected from the center of flow on a monthly basis as well as during selected storm events into pre-baked amber 125 mL glass bottles, put immediately on ice, and shipped overnight to the NWQL in Denver, CO. Samples for Biological Oxygen Demand (BOD) will also be collected monthly and during selected storm events, put immediately on ice, and driven to the Maryland Department of Health and Mental Hygiene (DHMH) Laboratory in Baltimore, MD. BOD samples collected during a stormflow event will usually come from the automatic sampler.

Sampling and analytical methods for trace metals

Samples for total recoverable and dissolved metal analysis will be collected using Clean Hand/Dirty Hand techniques and following protocols outlined in Chapter A4 of the USGS National Field Manual (U.S. Geological Survey, 1997 to present). Samples collected manually and by the automatic sampler will be composited in a pre-cleaned, acid-rinsed churn splitter, collected into acid-washed HDPE bottles, and preserved with Ultrex-brand nitric acid. Samples will be shipped on ice overnight to the NWQL in Denver, CO. Methods and reporting limits for trace metals are listed in Table 2.

USGS Watstore Code	Constituent (µg/L) and Method	Reporting Limit
01105 / 01106	Total Recoverable (ICPMS) / Dissolved Aluminum (ICPMS)	2 / 1.6
01002 / 01000	Total Recoverable (GFAA) / Dissolved Arsenic (ICPMS)	1.9 / 0.2
01027 / 01025	Total Recoverable (ICPMS) / Dissolved Cadmium (ICPMS)	0.04 / 0.04
01034 / 01030	Total Recoverable (GFAA) / Dissolved Chromium (GFAA)	0.8 / 0.8
01037 / 01035	Total Recoverable (ICPMS) / Dissolved Cobalt (ICPMS)	0.016 / 0.014
01042 / 01040	Total Recoverable (ICPMS) / Dissolved Copper (ICPMS)	0.6 / 0.4
01045 / 01046	Total Recoverable (ICPMS) / Dissolved Iron (ICPMS)	9 / 6.4
01051 / 01049	Total Recoverable (ICPMS) / Dissolved Lead (ICPMS)	0.06 / 0.08
01055 / 01056	Total Recoverable (ICPMS) / Dissolved Manganese (ICPMS)	0.2 / 0.2
01067 / 01065	Total Recoverable (ICPMS) / Dissolved Nickel (ICPMS)	0.16 / 0.06
01092 / 01090	Total Recoverable (ICPMS) / Dissolved Zinc (ICPMS)	2 / 0.6

Table 2. Methods and reporting limits for trace-metal analyses, NWQL Schedule 1849.

Sampling and analytical methods for suspended sediment

Samples for suspended-sediment analyses will be collected following protocols outlined in Chapter A4 of the USGS National Field Manual (U.S. Geological Survey, 1997 to present). Samples collected manually will be composited in the churn splitter, and collected into sediment bottles prior to shipment. Samples collected with auto-samplers are collected into a 1-L bottle specifically for SSC analyses. Suspended sediment concentration (SSC) is determined by gravimetric analysis. Samples for sand-fine split analysis are sieved prior to gravimetric analysis. Samples for loss on ignition (LOI) are dried in a muffle furnace at 550° C. Reporting limits for suspended sediment are listed in Table 3.

USGS Watstore Code	Constituent	Reporting Limit
80154	Suspended Sediment Concentration, SSC (mg/L)	1
70331	Sand-Fine Split, percentage finer than 0.063 mm	-
00535	Loss on Ignition, LOI (mg/L)	1
00530	Total Suspended Solids, TSS (mg/L)	10

Table 3. Methods for suspended-sediment analyses, USGS Kentucky District Sediment Laboratory.

Sampling and analytical methods for organics

Samples for organic contaminant analysis will be collected in the field through the use of automated samplers. Each water sample will be analyzed for polychlorinated biphenyls (PCBs), as 84 individual congeners, polycyclic aromatic hydrocarbons (PAHs), as 16 homologues, and organochlorine insecticides (OCIs), as 13 individual pesticides. The water samples will be retrieved from the auto-samplers immediately following a stream sampling event, and transported to the George Mason University (GMU) Environmental Chemistry Laboratory for analytical processing. The samples will be stored at 5 degrees Celsius in a cold room and extracted within 36 hours of collection. The stored samples are filtered through Gelman A/E glass fiber filters to separate dissolved and suspended matter in each water sample. PCBs, PAHs, and OCIs in filtered water (i.e., dissolved phase) are extracted into dichloromethane (DMC) using the Goulden large-sample extractor (Foster and Rogerson 1990; Foster et al. 1993), and are extracted from filter media (i.e., particulate phase) into DCM using Soxhlet extractors. Extracts from GLSE and Soxhlet extraction are subjected to column chromatography to isolate PCBs, PAHs, and OCIs into compound class fractions (Foster et al 2000a), where PAHs are analyzed using capillary gas chromatography/mass spectrometry, and PCBs and OCIs are analyzed using dual-column capillary gas chromatography-electron capture detection. Quality assurance is assessed through lab and field blanks, surrogate standards, matrix spikes and standard reference materials (sediments) as described previously (Foster et al. 2000b; Foreman et al. 2000). Methods and reporting limits are listed in Table 4. A detailed organics scope of work has been prepared by George Mason University and is attached.

USGS Watstore Code	Constituent (ng/L)	USGS Method	USEPA Method	Reporting Limit
NA	PCBs (84 congeners)	NA	8082 modified	0.1
NA	OC Insecticides (13 constituents)	NA	8081A modified	0.05
NA	PAHs (16 homologues)	NA	8100 modified	0.1

Table 4. Methods and reporting limits for organics, George Mason University Environmental Chemistry Laboratory, Fairfax Va.. (NA – not applicable.)

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Sampling and analytical methods for fecal indicator bacteria

Samples for fecal-indicator bacteria (*E. coli* and enterococci) will be collected from the center of flow using DHMH-supplied sterile bottles. Samples will be chilled immediately and driven to the DHMH laboratory in Baltimore, MD, within 6 hours of collection. Samples will be analyzed using Colilert and Enterolert methodology in order to meet compliance criteria for regulatory purposes.

After each sampling trip, all sample collection equipment, including sample collection bottles, churn splitters, and tubing is washed with a Liquinox solution, thoroughly rinsed with tap water, two rinses of distilled water, rinsed with 10% HCL and a final rinse of distilled water. The equipment is stored in clean plastic bins in order to minimize contamination during storage.

Field measurements

Field measurements will be made at the same time that water-quality samples are collected. Specific conductance, pH, dissolved oxygen, and water temperature, and turbidity will be determined with a calibrated multi-meter. Methods for field analysis are documented in the USGS National Field Manual (U.S. Geological Survey, 1997 to present).

Sample analysis, quality assurance, and quality control

All nutrient, trace metal, TOC, and TSS analyses will continue to be done at the NWQL in Denver, CO. Suspended-sediment analyses (including total suspended-sediment concentration, or SSC, LOI, and sand-fine fractionation) will be done at the USGS Kentucky District Sediment Laboratory. Approximately one-third of the samples will be selected and analyzed for SSC, LOI, and percent fines, while two-thirds will be analyzed only for SSC. BOD analysis will be performed at DHMH. Organics analysis will continue to be conducted at the GMU Laboratory in Fairfax, Va.

USGS will provide quality assurance and quality control oversight for water-quality samples. The primary quality-assurance objectives will be to control bias due to equipment contamination and poor sampler-intake efficiency, evaluate sample collection techniques and potential problems with laboratory performance, and estimate data precision. Due to a limited number of samples being collected, meaningful quality assurance through statistical process control is not possible. Quality-assurance procedures for sample collection will consist of using appropriate equipment cleaning and sample-collection techniques prescribed by Wood and Harr (1990) and Edwards and Glysson (1988) and submitting quality-control samples.

Quality-control samples will consist of equipment blanks, field blanks, field-split duplicates, and comparisons of the automatic sampler to the river cross-section. Field blanks and field replicates will be collected to monitor bias and precision in all aspects of data collection. Equipment blanks will provide data on sample contamination and will be collected using certified inorganic-free water; the ISCO automatic sampler blanks will be collected prior to field deployment as well as in situ. Field-split duplicates provide a measure of analytical precision on environmental samples and will be collected for base-flow and stormflow samples. Comparisons of the automatic sampler to the river cross section provide a measure of bias due to the location of the intake for the automatic sampler and the potential for loss of heavier solids during pumping to the sampler, and will be collected over a range of flow conditions.

Coordination of sampling events and sampling frequency

Storm samples - USGS will select storms targeted for sampling and appropriately program the automatic sampler. USGS will collect discrete storm samples and maintain the samplers. After the storm event, USGS will review the hydrograph and select samples to be analyzed. GMU operates and maintains separate ISCO storm samplers, and will continue to collect composite storm samples using their equipment. USGS and GMU will coordinate sampling efforts wherever possible.

Baseflow and high-flow grab samples - USGS will select dates for baseflow and high-flow grab samples. Discharge will be recorded at the time of sample collection for the high-flow samples.

Sampling frequency - USGS and GMU will collect and analyze approximately 12-50 samples per water year from a site, depending on the constituent and is contingent upon availability of funding (see Table 5), including samples required for quality assurance and quality control. Samples will be collected over a range of hydrologic conditions and seasons.

Constituent	Lab	Approximate Number of Samples per Site per Year
Nutrients (N, P)	NWQL	40-50
BOD	DHMH	12-18
TSS	NWQL	40-50
SSC	Kentucky	40-50
SSC-Sand-Fine Break	Kentucky	20
LOI	Kentucky	20
Metals (Total Recoverable & Dissolved)	NWQL	40-50
TOC	NWQL	12-18
<i>E. Coli</i> / enterococci	DHMH	12-18
Organics (PCBs, PAHs, pesticides; dissolved and particulate phases)	GMU	25

Table 5. Summary of analytes, labs, and sampling frequency.

Characterization of Surface-Water Quality through Continuous Data Collection and Regression Analysis

USGS has pioneered new methods of characterizing surface-water quality through use of multi-parameter probes combined with simultaneous sampling and analysis (Christensen, 2001; Christensen, Jian, and Ziegler, 2000). Through application of multiple regression techniques, statistically significant relations may be developed between continuous variables measured by probe sensors and concentrations of various constituents measured in discrete samples. If discrete water-quality sampling and real-time data collection of water temperature, specific conductance, pH, and turbidity continues beyond 2006, this would allow for continuous estimation of constituent concentrations and real-time data presentation. With continuous flow data and concentration estimates, determinations of chemical loadings over a given time period (for example, during a storm) are made possible.

Sites will be instrumented with a suite of sensors that will continuously measure and record water temperature, specific conductance, turbidity, and pH, at 15-minute intervals. Continuous dissolved-oxygen data will be displayed depending on the quality of the record. The nutrient concentration values determined from samples collected at a site (described above) will be related to concurrent values of these measured parameters to estimate (when possible) nitrate, total nitrogen, total phosphorus, bacteria, and suspended-sediment concentrations in the stream water at 60-minute intervals. The load for each time interval will be calculated by multiplying the estimated concentration by the discharge for the interval computed from the stage-discharge relation established for the site. Total loads for any given period of time can be calculated by summing the loads computed for each measurement interval during the specified period. The accuracy of the continuous water-quality sensors will be checked on a monthly basis and corrected for any detected drift. Probe maintenance will also be performed monthly, including inspection and cleaning to remove organic films and sediment.

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Hydrological Systems Analysis

Load estimation and analysis

USGS has significant experience with estimation of delivered loads, through the River Inputs Monitoring Program (Belval and Sprague, 1999) and other programs. USGS typically uses the ESTIMATOR program, developed by Tim Cohn (Yochum, 2000), a seven-parameter regression model, for load estimation, although other methods may be applied in some cases (Preston and Summers, 1997). Load estimation typically requires at least three years of data collection, with at least 18-24 samples each year. Significantly longer time periods are required to assess trends in loads. For example, the River Inputs Monitoring Program uses a nine-year moving window to calculate a single annual load (for the middle year), and a twelve- to sixteen-year record for analysis of trends.

Monthly and annual loads will be estimated for major constituents (nitrogen and phosphorus species, suspended sediment), using the ESTIMATOR program. These load estimates may be compared with those from regression analysis of continuous surrogate data (see above). Trends may eventually be evaluated, after several years of data collection, using output from ESTIMATOR (flow-adjusted concentration trend) or through Seasonal Kendall testing of monthly flows and loads and flow-weighted concentrations (Langland, Blomquist, and others, 2000). Loads for organics data will be estimated by George Mason University under the terms of the contract for organics data collection and analysis.

Products

The data-collection phase of the project will run from July 2003 through June 30, 2006. Primary products from the project will be water-quality data that will be published on a water-year basis in annual data reports by the USGS. In addition, USGS will provide semi-annual progress reports to PGC and MDE (due June 30 and December 31 for each project year). Data collected by GMU for organics will be forwarded from USGS to PGC and MDE. An interpretive report will be completed in FY 2007 (project year 4).

References

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