Prepared in cooperation with
Prince George's County Department of Environmental Resources
the Maryland Department of the Environment
the U.S. Environmental Protection Agency
and George Mason University

Water Quality in the Upper Anacostia River, Maryland: Continuous and Discrete Monitoring with Simulations to Estimate Concentrations and Yields, 2003–05

Scientific Investigations Report 2007–5142

U.S. Department of the Interior
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Cover. The historical stream gage at the Northeast Branch Anacostia River at Riverdale, Maryland (USGS Station 01649500). (Photograph by U.S. Geological Survey)

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Suggested citation:
Miller, C.V., Gutiérrez-Magness, A.L., Feit Majedi, B.L., and Foster, G.D., 2007, Water quality in the Upper Anacostia River, Maryland: Continuous and discrete monitoring with simulations to estimate concentrations and yields, 2003–05: U.S. Geological Survey Scientific Investigations Report 2007–5142, 43 p.

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Conversion Factors

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km^2)	247.1	acre
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic meter per second (m^3/s)	70.07	acre-foot per day (acre-ft/d)
cubic meter per second (m^3/s)	22.83	million gallons per day (Mgal/d)
millimeter per year (mm/yr)	0.03937	inch per year (in/yr)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)
kilogram (kg)	0.0011	ton (short, 2,000 lb)
	Yield rate	
kilogram per year per square kilometer ($kg/yr/km^2$)	0.00286	ton per year per square mile ($tn/yr/mi^2$)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Concentrations of chemical constituents on suspended particulates are given in milligrams per kilogram (mg/kg) of dry weight of the suspended particles.

Units of turbidity are given in formazin nephelometric units (FNU), which are nephelometric turbidity units based on a formazin standard.

Water year is the 12-month period starting October 1, and ending September 30 of the following year.

Water Quality in the Upper Anacostia River, Maryland: Continuous and Discrete Monitoring with Simulations to Estimate Concentrations and Yields, 2003–05

By Cherie V. Miller, Angélica L. Gutiérrez-Magness, Brenda L. Feit Majedi, and Gregory D. Foster

Abstract

From 2003 through 2005, continuous and discrete water-quality data were collected at two stations on the Anacostia River in Maryland: Northeast Branch at Riverdale, Maryland (U.S. Geological Survey Station 01649500) and Northwest Branch near Hyattsville, Maryland (Station 01651000). Both stations are above the heads of tide for the river, and measurements approximately represent contributions of chemicals from the nontidal watersheds in the Anacostia River. This study was a cooperative effort between the U.S. Geological Survey, the Prince George's County Department of Environmental Resources, the Maryland Department of the Environment, the U.S. Environmental Protection Agency, and George Mason University. Samples were collected for suspended sediment, nutrients, and trace metals; data were used to calculate loads of selected chemical parameters, and to evaluate the sources and transport processes of contaminants. Enrichment factors were calculated for some trace metals and used to interpret patterns of occurrence over different flow regimes. Some metals, such as cadmium, lead, and zinc, were slightly enriched as compared to global averages for shales; overall, median values of enrichment factors for all metals were approximately 15 to 35.

Stepwise linear regression models were developed on log-transformed concentrations to estimate the concentrations of suspended sediment, total nitrogen, and total phosphorus from continuous data of discharge and turbidity. The use of multiple explanatory variables improved the predictions over traditional rating curves that use only streamflow as the explanatory variable, because other variables such as turbidity measure the hysteretic effects of fine-grained suspended sediment over storm hydrographs. Estimates of the concentrations of suspended sediment from continuous discharge and turbidity showed coefficients of determination for the predictions (multiple R^2) of 0.95 and biases of less than 4 percent. Models to estimate the concentrations of total phosphorus and total nitrogen had lower values of multiple R^2 than suspended sediment, but the estimated bias for all the models was similar. The models for total nitrogen and total phosphorus tended to under-predict high concentrations and to over-predict low concentrations as compared to measured values.

Annual yields (loads per square area in kilograms per year per square kilometer) were estimated for suspended sediment, total nitrogen, and total phosphorus using the U.S. Geological Survey models ESTIMATOR and LOADEST. The model LOADEST used hourly time steps and allowed the use of turbidity, which is strongly correlated to concentrations of suspended sediment, as a predictor variable. Annual yields for total nitrogen and total phosphorus were slightly higher but similar to previous estimates for other watersheds of the Chesapeake Bay, but annual yields for suspended sediment were higher by an order of magnitude for the two Anacostia River stations. Annual yields of suspended sediment at the two Anacostia River stations ranged from 131,000 to 248,000 kilograms per year per square kilometer for 2004 and 2005. LOADEST estimates were similar to those determined with ESTIMATOR, but had reduced errors associated with the estimates.

Introduction

Urban streams are particularly complex systems with physical and chemical stressors that often overshadow natural stream processes and functions. Some typical physical stressors in urban streams include increases in impervious surface in the watershed, trash, and in-stream structures such as dams, weirs, and riprap that alter the physical form of the stream. Chemicals can enter streams from sewage-treatment outfalls, leaking underground sewer infrastructure, industrial outfalls, landfills, nutrient and pesticide applications for lawns and right-of-ways, residues that wash off paved surfaces, and the atmosphere. The effects of elevated chemicals in urban streams are often detrimental. Some chemicals such as pesticides and metals can cause toxicity, and excess nutrients can enhance productivity to the point of eutrophication in the stream. Nevertheless, urban streams survive and may even flourish, albeit often in states that are altered from natural conditions. The benefits of restoration and preservation of urban streams are not just for aesthetics; these environments support an ecology that extends well beyond the local urban area. The Chesapeake Bay Basin is a good example, where years of study have demonstrated the importance of contributions from the nontidal tributaries to a healthy estuary (U.S. Geological Survey, 2006).

The Anacostia River is an important urban stream in Washington, D.C. and Maryland, and is a tributary to the Chesapeake Bay. The lower reaches of the Anacostia River are within the city limits of Washington, D.C. Most of the lower reaches are tidally influenced, and are surrounded by dense urban land use. The tidal Anacostia River is listed as one of three Regions of Concern by the U.S. Environmental Protection Agency's Chesapeake Bay Program (CBP) (Chesapeake Bay Program, 1999). The upper watershed is situated in Montgomery and Prince George's Counties in Maryland. Although these counties are still experiencing rapid growth and development, they are less densely urbanized than the tidal reaches in Washington, D.C. Local governments in Washington, D.C. and the surrounding counties are working to improve conditions in the Anacostia River and submit an annual plan for improvement to the CBP.

Purpose and Scope

The purpose of this report is to summarize the results of a study by U.S. Geological Survey (USGS) on the water quality in the upper Anacostia River watershed. The USGS study has quantified the contributions of suspended sediment (SS) and chemicals from the upper watersheds in Maryland, and used these data to interpret transport processes and the magnitudes of loadings to the more heavily urbanized tidal area. USGS has developed a cooperative program to work on the Anacostia River with other scientific agencies and jurisdictions including the Prince George's County Department of Environmental Resources, the Maryland Department of the Environment, the U.S. Environmental Protection Agency, and George Mason University.

This study focused on two monitoring stations near the Maryland/Washington, D.C. border that are immediately upstream of the head of tide in the Anacostia River. Water-quality data were collected to measure: (1) discrete concentrations of nutrients, dissolved and total-recoverable trace metals, and SS, and (2) continuous water temperature, pH, specific conductance, concentration of dissolved oxygen, and turbidity over a 2-year period. The discrete data were evaluated to determine the primary phases of nutrients and metals in transport, the behavior of SS and chemicals over time and varying flow regimes, and enrichment factors (EFs) for trace metals in SS. Unbiased regression models were developed to estimate annual yields of SS, total nitrogen (TN), and total phosphorus (TP) at each station. Regression models were used to estimate the concentrations of SS, TN, and TP from continuous parameters.

The data from this study have provided insights into the contributions of potential contaminants from the upper watershed of the Anacostia River. These data may be compared to data collected in the lower tidal Region of Concern in the Anacostia River as well as to other tributaries in the Chesapeake Bay watershed, and urban streams across the United States. Estimation of the quantities and comparative magnitudes of contaminants within the context of transport processes in the river system will aid water-resource managers in focusing management strategies where improvements may be most beneficial and cost-effective. The following objectives outline the goals of this study:

1. Water-quality data were collected, summarized, and described over a 2-year period at the Northeast and Northwest Branches of the Anacostia River (USGS water-quality and gaging stations 01649500 and 01651000, respectively), and included nutrients, trace metals, and SS. Samples for organic compounds and bacteria were collected concurrently for this study but are not described in this report.
2. Annual yields (loads per square area) for SS, TN, and TP for both Anacostia River stations for calendar years 2004 and 2005 were estimated.
3. Statistical relations from continuous water-quality and -quantity measurements (discharge, water temperature, pH, specific conductance, turbidity, and concentration of dissolved oxygen) were developed to estimate the concentrations of SS, TN, and TP.
4. Observations of water chemistry in terms of fluvial and urban processes in the upper nontidal Anacostia River are presented.

Description of the Anacostia River and Watershed

The Anacostia River flows through an urban corridor in central Maryland and Washington, D.C. (figs. 1A–C). Climate in this area is temperate with an average annual rainfall in Maryland of approximately 45 inches (National Oceanic and Atmospheric Administration, 2002). The Anacostia River watershed extends into Montgomery and Prince George's Counties in Maryland and down to the Potomac River. The tidal portion of the Anacostia River is mainly within the boundaries of Washington, D.C. The stations selected for this study are the Northeast Branch Anacostia River at Riverdale, Maryland (USGS Station 01649500; fig. 2) and the Northwest Branch Anacostia River near Hyattsville, Maryland (USGS Station 01651000; fig. 3). The two stations are just above the highest points of tidal influence in the Anacostia River, which occurs near the boundary between Maryland and Washington, D.C. The two branches reach a confluence in the

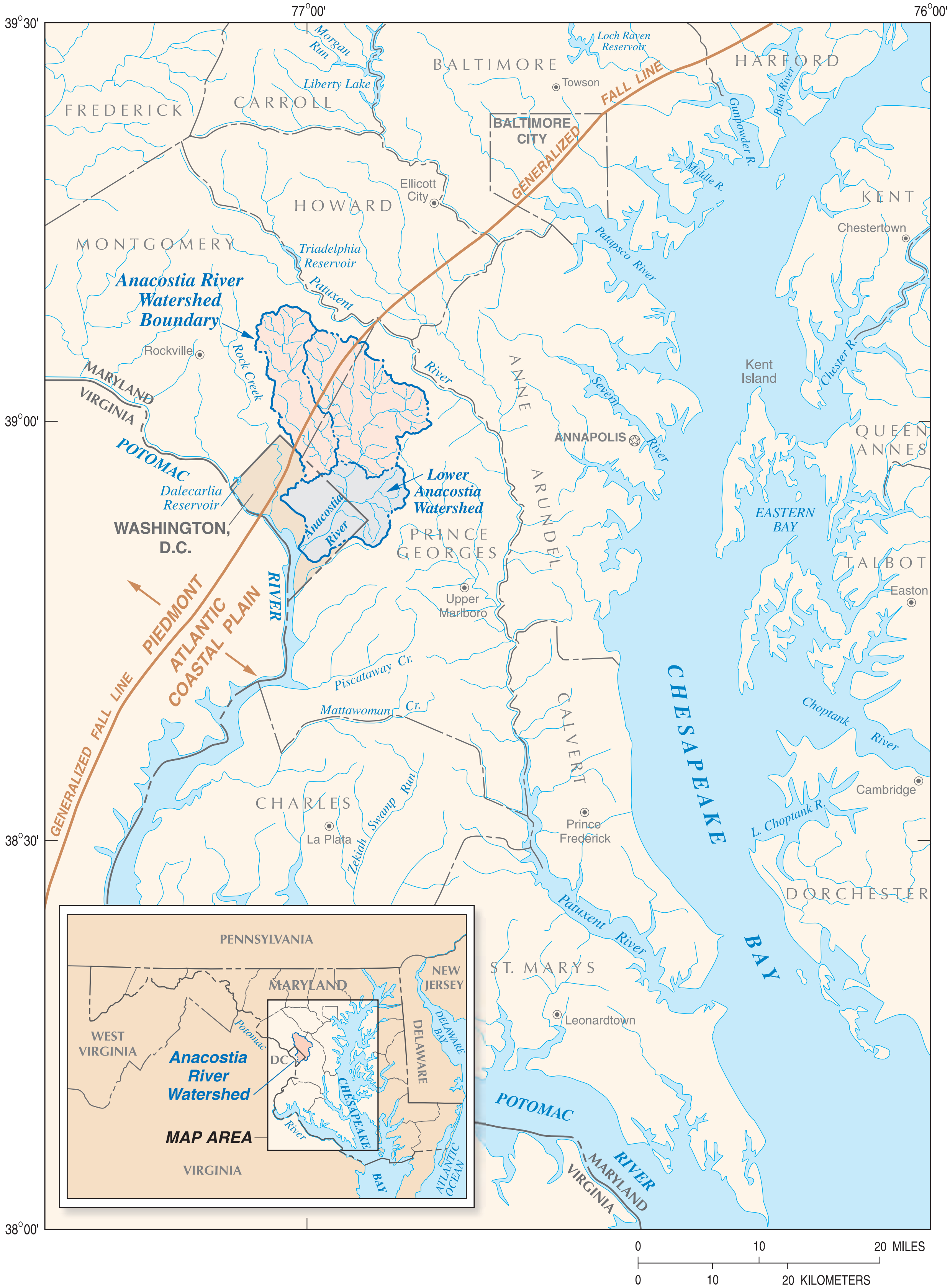

Figure 1A. Location of the Anacostia River watershed, which includes the lower watershed which is partially tidal within Washington, D.C., and the upper watershed in Maryland.

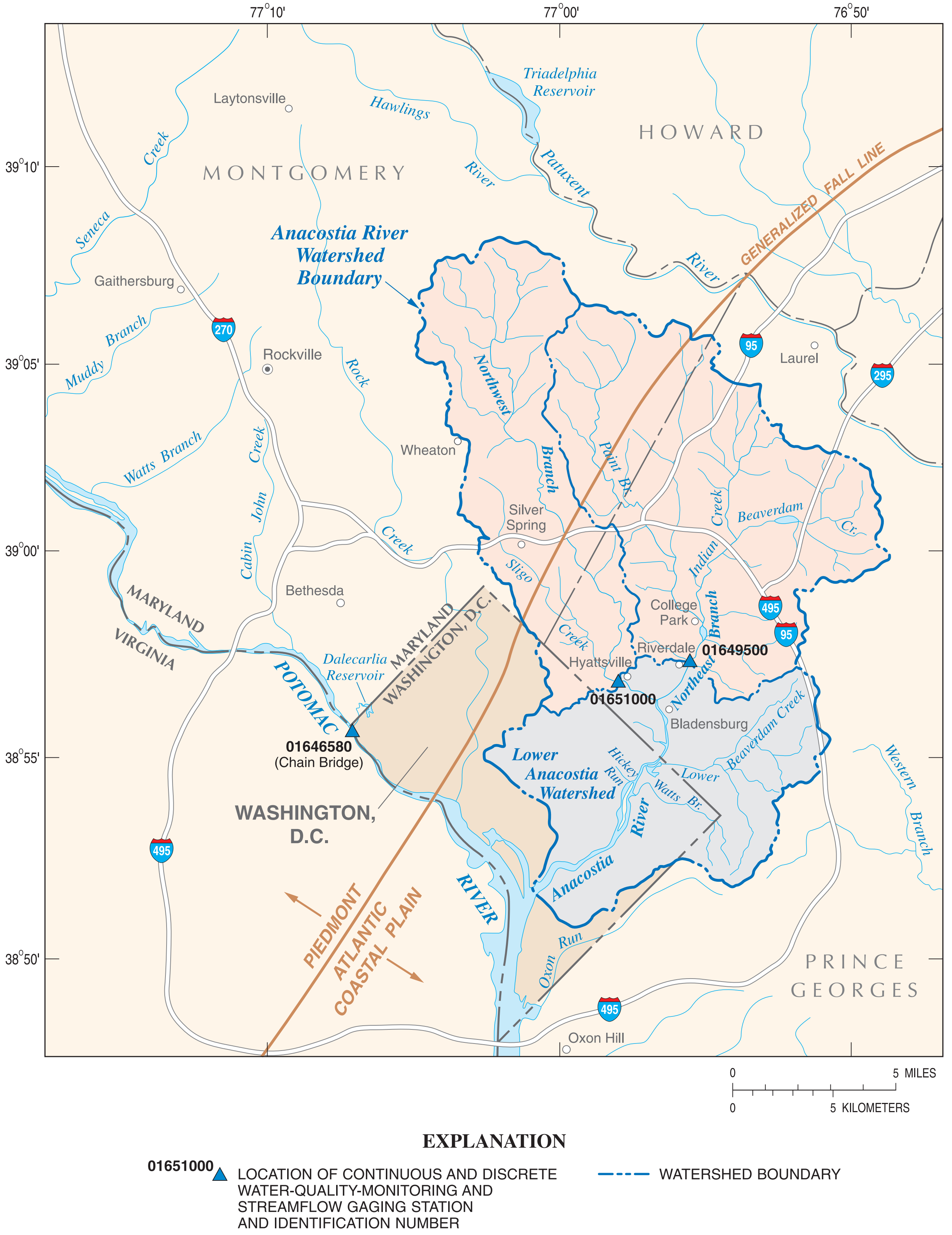

Figure 1B. Detailed view of the Anacostia River watershed. The upper watershed of the river includes the Northeast Branch and the Northwest Branch of the Anacostia River.

Figure 1C. Location of the Anacostia River watershed and the dominant hydrogeomorphic regions in the upper watersheds of the Northeast and Northwest Branches (USGS stations 01649500 and 01651000, respectively). (Modified from Reger and Cleaves, 2003.)

Figure 2. The historical stream gage (at left end of bridge) at the Northeast Branch Anacostia River at Riverdale, Maryland (USGS station 01649500). (Photograph by U.S. Geological Survey)

Figure 3. View upstream of the water-quality sampling station at the Northwest Branch Anacostia River at Hyattsville, Maryland (USGS station 01651000). (Photograph by U.S. Geological Survey)

Anacostia River at Bladensburg Maryland, just below the two sampling stations. Bladensburg served as a major seaport for Washington, D.C. until the mid-1800s, when sediment from erosion due to agriculture and development made most of the Anacostia River non-navigable (Williams, 1977; Gottschalk, 1945). Many changes, particularly to the tidal channels, have occurred since then, and the modern-day Anacostia River is very different from colonial times. From the latter part of the 1900s to the present, urbanization has increased throughout the watershed and is the most dominant influence on the river. Since about 1987, efforts have been made to restore and improve conditions on the Anacostia River.

The two main physiographic provinces of the Anacostia River Basin are the Piedmont Plateau and the Atlantic Coastal Plain (fig. 1C). The upper part of the Anacostia watershed lies in the Piedmont Upland Section, specifically in the Hampstead Upland District, which is within the Harford Plateaus and Gorges Region (Reger and Cleaves, 2003). The Piedmont Upland is comprised of rolling hilly terrain with distinctive ridges, hills, and valleys and moderately thin soil zones. The Atlantic Coastal Plain consists mainly of alluvium, with generally flatter topography of sedimentary beds and thicker soil zones than that of the Piedmont Plateau. Slopes in the Atlantic Coastal Plain are usually less than 8 degrees. Lithologies in this area of the Atlantic Coastal Plain are mainly quartzitic and sometimes micaceous sands, gravels, silts, and clays. River valleys are incised into the Atlantic Coastal Plain alluvium; delineated in the Anacostia Valley Area in figure 1C. The river valleys consist mainly of gently dipping quartzitic and micaceous sediments with gently dipping beds, and locally there are Tertiary terraces on either side of the main channels. The Fall Zone is a region of the Piedmont Plateau, a transition area between the Piedmont Plateau and the Atlantic Coastal Plain, where there is often an abrupt change in slope. In the study area, the Fall Zone is described by Reger and Cleaves (2003) as the Perry Hall Upland District. Bedrock in the Fall Zone is a mixture of metagabbros and granites unconformably overlain by alluvium. The hilltops are often capped with Cretaceous sediments, mainly gravels and sands; rivers may incise down to the bedrock (Reger and Cleaves, 2003).

Land cover in the watersheds above the two sampling stations is shown in figure 4. The land-cover classes are grouped so that the developed category includes all urban and suburban development; commercial, industrial, and residential areas of all densities and areas with and without trees and(or) ground cover. Major point-source dischargers that are permitted through the National Pollutant Discharge Elimination System (NPDES) Permitting Program are shown in figure 4 (Frank Siano, MDE, written commun., 2006). Two of the NPDES sites are municipal wastewater-treatment plants operated by the U.S. Department of Agriculture. The other point sources in the study area include light industrial waste (some sources of metals such as paint pigments and metal electroplating), petroleum hydrocarbons from parking and other commercial facilities, and mixed waste from military facilities. The land-use category of agriculture includes row and grain crops, pasture, and orchards. Forested areas include all undeveloped land, and barren areas include quarries and other areas without ground cover.

There is a strong influence from various types of development in both watersheds (fig. 4)—the percent of impervious surface throughout the watershed areas further emphasizes this point (fig. 5). Impervious surfaces are defined as man-made areas such as paved areas and roofs that do not readily absorb or retain water. These areas can have a negative effect on the biotic integrity of streams because of increases in the velocity and quantity of flow during storms and subsequent deterioration of channel stability and aquatic habitat. Arnold and Gibbons (1996) proposed a threshold of about 10-percent impervious surface for observable declines in stream integrity. The concept of a threshold is actually variable and not always clearly defined, but the percent of impervious surface can be an important overall indicator of urban influences. Whereas the average percentage of impervious surface in the Anacostia River watershed is about 20 percent, higher percentages are concentrated in the lower parts of the watershed. Impervious surfaces influence flow, as well as the quantities of chemicals that are transported. Stormwater-management controls can alleviate some of the impacts of impervious surfaces, but it is often difficult to implement these controls at or above the usual rate of urban and suburban development.

Several consortia with many local and Federal partners have been formed to develop and implement a plan for the restoration of the Anacostia River; the Anacostia Watershed Toxics Alliance (AWTA) (Anacostia Watershed Toxics Alliance, 2001) and the Anacostia Watershed Restoration Committee (AWRC) (Metropolitan Washington Council of Governments, 1998, 2003) continue to report progress on these efforts. Several major stream-restoration projects, both upstream and downstream of the sampling station on the Northwest Branch, were ongoing during the current study (2003–05) and had the potential to influence the amount of sediment that was transported (fig. 6). Stream-restoration projects in the Northwest Branch Anacostia River were completed by December 2004.

Hydrology in the nontidal portion of the Anacostia River can be described as flashy with a quick, relatively short storm response and a lot of energy during high-flow events. Conversely, the tidal Anacostia River within Washington, D.C. is more sluggish, and a lot of the sediment that is transported from Maryland is deposited in the upper tidal river and mudflats where flow is slower, allowing settling and deposition of the suspended sediment. Tidal waters of the Anacostia River below Bladensburg have a mean residence time on the order of 35 days (Velinsky and others, 1994).

Contaminants in the Anacostia River

Most of the contaminants in the Anacostia River occur in the lower tidal portion within Washington, D.C., which is listed as one of three Regions of Concern by the CBP. Segments of the river in this area are listed on Maryland's

Figure 4. Land cover in the Anacostia River watershed (Hitt, 2006). Industrial and municipal discharge sites are permitted through the National Pollutant Discharge Elimination System (NPDES).

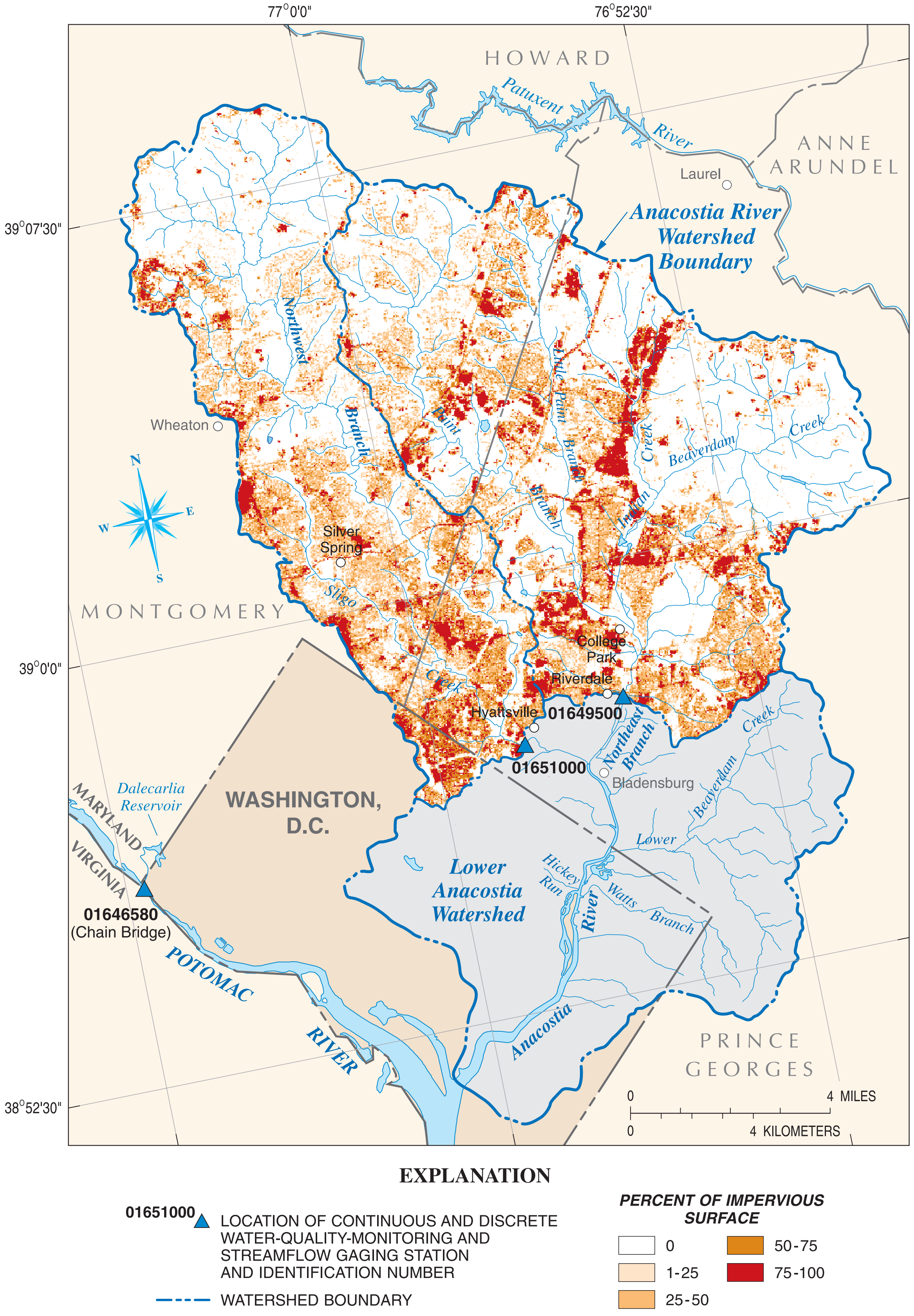

Figure 5. Percent of impervious surface in the Anacostia River watershed (Smith and others, 2002).

Figure 6. Stream-restoration project by the Maryland State Highway Administration on the Northwest Branch Anacostia River (USGS station 01651000), August 7, 2003. (Photograph by U.S. Geological Survey)

303(d) list for a number of contaminant issues, including bacteria, biological integrity, polychlorinated biphenyls (PCBs), and the pesticide heptachlor epoxide. Since the late 1980s, a number of organizations such as the AWRC and AWTA have been formed to facilitate the rehabilitation of the Anacostia River and watershed. The membership of these organizations includes Federal, State, and County governments, as well as a number of citizens groups. Organizations such as the "Anacostia Watershed Society" and the "Friends of Sligo Creek" use volunteers to conduct clean-up and monitoring efforts and to educate the public about the status of their local streams. Recent improvements in the Anacostia River include wetland and riparian-zone restoration, trash and debris reduction, replacement of leaking sewer infrastructure, and Low-Impact Development (LID) that uses passive engineering improvements to redirect and process storm runoff (Metropolitan Washington Council of Governments, 1998, 2003; Anacostia Watershed Toxics Alliance, 2001).

Recent studies by Pinkney and others (2001, 2004) have reported severe chemical effects on brown bullhead in the lower tidal Anacostia River. They observed metabolites of polycyclic aromatic hydrocarbons (PAHs) in bile, DNA adducts of PAHs in liver tissue, PCBs, and organochlorine pesticides in muscle tissue, and used cytochrome P450 (ethoxyresorufin-O-deethylase or EROD assay) in liver to link observations of barbel malformations and tumors to exposure to organic chemicals. They concluded that the likely causative chemicals for the observed diseases in brown bullhead in the Anacostia River were PAHs, dichloro-diphenyl-trichloroethane (DDT), PCBs, and(or) chlordanes.

Sedimentation has been a continuous problem in the Anacostia River over the last 200 years as the land surface in the watershed has been cleared for development. Williams (1977) documented significant narrowing of the channel from Bladensburg, Maryland, down to the Washington, D.C. border during this period, with increasing rates of sedimentation during the 1900s. Yorke and Herb (1978) documented large increases in land clearing in the upper Northwest Branch of the Anacostia during the 1960s and 1970s with a large shift in land use to suburban and urban. An important effect of urbanization is the increase in peak stormflows due to increases in impervious surface in the watershed and hard channelization of the streambeds. Increased peak storm velocities can accelerate the rates of erosion of streambanks, thus augmenting sediment loads. Yorke and Herb (1978) documented increased sediment loads in the more urbanized areas of the watershed and showed that most of the load was transported during storm events—73 percent in 2.2 percent of the time, and 94 percent in 5.7 percent of the time. Loads of sediment were variable between storms and were correlated to the volume and peak discharge of the storm runoff. York and Herbe (1978) determined that major sources of sediment in the watersheds were cropland, urban land, and construction sites, although more recent laws governing sediment-control structures at construction sites would be expected to reduce some of these effects. Studies such as Horowitz and others (in press) have shown that antecedent conditions such as the length and intensity of dry periods between storms as well as the strength of preceding storms affect the quantities of sediment and chemicals that are mobilized during each storm.

Methods of Study

Two types of water-quality and quantity data were collected at the sampling stations on the Northeast and Northwest Branches of the Anacostia River: (1) continuous measurements for discharge, pH, water temperature, specific conductance, concentration of dissolved oxygen, and turbidity were collected from January or February 2004 through December 2005; and (2) discrete measurements of the concentrations of nutrients, SS, and trace metals were collected from July 2003 through December 2005. All data were archived in the USGS National Water Information System (NWIS) database and are available upon request from the USGS Maryland-Delaware-D.C. Water Science Center (MD-DE-DC WSC) in Baltimore, Maryland.

Field methods described in this report are documented in the USGS National Field Manual (NFM) for the collection of water-quality data (U.S. Geological Survey, variously dated) and Guidelines and Standard Procedures for Continuous-Water-Quality Monitors (Wagner and others, 2006). Chapters of the NFM are updated on a continuous basis and are available on the world wide web.

Measurements of Continuous Flow and Water Quality

Continuous-flow measurements were estimated from river stage that was recorded using a stilling well and float recorder. The gage height was recorded every 15 minutes, individual measurements of flow were made throughout the range of stages, and a stage-discharge relation was maintained to create a record of continuous flow. The stations at both the Northeast and Northwest Branches of the Anacostia River have operated continuously from 1938 to the present.

Continuous measurements for water temperature, specific conductance, pH, concentration of dissolved oxygen, and turbidity was performed using YSI model 6600 multiparameter data sondes that were deployed in the river. The data sondes reported readings of each parameter collected at 15-minute intervals to an onsite electronic CR10X data logger, which stored the data for transmission to the USGS at 4-hour intervals. Continuous data were reported in near-real time on the world wide web at *http://waterdata.usgs.gov/md/nwis/current/?type=quality*.

To collect accurate and precise data, equipment at both sites was field inspected and calibrated at intervals ranging from 1 to 6 weeks as dictated by hydrologic conditions, data-transmission quality (fouling and drift), and the known functional limitations of the equipment. For cleaning and calibration of the monitor and sensors, multiple observations of each parameter were made during the entire process, and were used to determine separate corrections for both fouling and drift. Standards for specific conductance were prepared and quality-assured at the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado. Standards for pH were manufactured by the Fisher Scientific Company. Formazin-based standards for turbidity were manufactured by YSI and were used without dilution. Shifts and corrections that exceeded acceptable criteria (Wagner and others, 2006) were applied to the continuous-data records in the USGS NWIS database after each field inspection was completed. Corrected (provisional data) were displayed in near-real time on the USGS webpage of the MD-DE-DC WSC. After review, data were published in the USGS Annual Water-Data Report series for water years (October through September) during which data were collected.

Field Collection of Water-Quality Samples

Discrete samples for water quality were collected from the streams during base-flow conditions using equal-width increment (EWI) sampling techniques (U.S. Geological Survey, variously dated). Multiple depth-integrated subsamples were collected at equal intervals across the stream (approximately 10 sections) and composited into an acid-washed polycarbonate churn splitter to collect a representative sample of the entire stream. The samples were processed within the housing at the streamflow-gaging station, in a clean USGS field van, or in the USGS MD-DE-DC WSC laboratory to avoid environmental contamination. Subsamples of whole water were dispensed while churning into clean polyethylene or glass bottles. After all whole-water samples had been collected, samples for dissolved analysis were collected from the churn using a peristaltic pump with an in-line acid-washed polycarbonate capsule filter [0.45 μm (micrometer) effective pore size]. Samples for total-recoverable and dissolved metals were fixed with 1 mL (milliliter) of Nitrix nitric acid to attain a pH of less than 2. Samples for whole-water analysis of nutrients were fixed with 1 mL of sulfuric acid. Samples for nutrients and metals were chilled to less than 4°C (degrees Celsius) and shipped on ice overnight to the USGS NWQL in Denver, Colorado. Samples for SS were stored and shipped later to the USGS Sediment Laboratory in Louisville, Kentucky.

An automatic sampler was installed at each station so that samples could be collected more frequently during storm events (fig. 7). Four to six samples were collected over each storm hydrograph, based on changes in flow and precipitation. Pressure transducers and rain gages were installed and connected directly to the autosamplers to provide information on stream conditions that would automatically trigger the autosamplers. Time-discrete samples were processed from selected points in the storm hydrograph. To compare methods for EWI and autosampling, several samples were collected

Figure 7. Automatic sampler with CR10X data logger and modem to record physical parameters, upload data in near-real time to the world wide web, and to trigger the sampler during storm events. (Photograph by U.S. Geological Survey)

simultaneously using both techniques. Field data for water and air temperature, pH, specific conductance, concentration of dissolved oxygen, and turbidity were recorded from a handheld YSI field meter (Model 600XL) at the time of each manual sampling event.

Laboratory Methods

Nutrients were analyzed at the USGS NWQL. Samples for total and soluble phosphorus and Kjeldahl nitrogen were digested concurrently in block digestors at high temperature with a mercury, Hg(II), catalyst. Ammonium ions, both those originally present and those generated by the procedure, were analyzed colorimetrically by a salicylate-hypochlorite Berthelot-reaction procedure using an air-segmented continuous-flow analyzer. Ammonia nitrogen was analyzed separately by the same colorimetric procedure, and organic nitrogen was determined by difference. Phosphate was analyzed in a separate aliquot from the same digestate using the ammonium-molybdate colorimetric method and automated segmented flow (Fishman, 1993; Patton and Truitt, 2000). Nitrite-nitrogen was analyzed by diazotization and colorimetric detection in automated segmented flow. Nitrate was reduced by cadmium metal and analyzed as nitrite to give total nitrate/nitrite-nitrogen (Fishman, 1993). Nitrate-nitrogen was determined by difference. Total nitrogen was calculated as the sum of total Kjeldahl nitrogen and total nitrate/nitrite nitrogen.

Metals were measured in the dissolved phase and as total recoverable by partial digestion at the NWQL. Samples for total-recoverable metals were prepared by whole-water in-bottle digestion with nitric acid (about 3 percent by volume). Acidified samples were incubated at 65°C for 8 hours and then filtered through a 0.45-µm filter. Samples for aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) were analyzed by direct-injection inductively coupled plasma-mass spectrometry (ICP-MS). Individual interferences for trace metals were controlled (Faires, 1992; Garbarino and Struzeski, 1998; Garbarino, 1999a,b; Garbarino and Hoffman, 1999; Garbarino and others, 2006). Aliquots for both dissolved and total-recoverable mercury (Hg) were analyzed separately using the cold-vapor method and atomic-fluorescence spectroscopy (Garbarino and Damrau, 2001). The total-recoverable digestion method extracts labile metals but does not dissolve silicates or other resistant mineral phases. All methods at the USGS NWQL are quality-assured by the National Environmental Laboratory Accreditation Program (NELAP), the USGS Branch of Quality Systems that conducts blind audits, and the USGS Standard Reference Sample (SRS) program.

Concentrations of SS and the percent of sediment that was finer than 0.63 µm were analyzed using filtration and gravimetric methods at the USGS Sediment Laboratory in Louisville, Kentucky. All methods and quality-assurance procedures for sediment analyses are documented in the laboratory quality-assurance plan (Shreve and Downs, 2005).

Evaluation of Data Integrity

Field blanks were collected and analyzed for trace metals, nutrients, SS, and total organic carbon. Most field blanks had concentrations less than the reporting levels or were not detected. In several instances, there were measurable concentrations in the field blanks but these values were very near the reporting limits and were almost always less than 10 percent of ambient concentrations. Total organic carbon had two blanks with concentrations of E0.3 and 0.5 mg/L (milligrams per liter). E-coded values are concentrations that are determined to be below the reporting level but above the detection level. These samples represent positive detections, but the values have a low precision. One blank for trace metals had a concentration of 17 µg/L (micrograms per liter) for total-recoverable Al, possibly indicating a problem with filtration in that sample, but all other values for metals in this sample were non-detects or less than the reporting limit. On August 24, 2005, the field blank from the Hyattsville site had a total-recoverable Zn concentration of 5 µg/L, which is above the reporting level of 2 µg/L, and is in the range of concentrations found in base-flow samples at both sites. Low-level concentrations of As, Fe, Mn, Cu and nutrients also were detected in this sample.

Approximately 10 percent of all samples were replicated to evaluate the precision of the methods. For most of the replicates, a second sample was pulled from the composite sample in the churn splitter. Relative percent differences for replications were well within plus or minus 3 percent for nutrients, 5 percent for metals, and 15 percent for the concentrations of SS, except where concentrations were near the reporting limits.

Some replicates compared different sampling methods such as autosampling from a point on the side of the stream with EWI sampling using either a D-81 or DH-95 integrated sampler (USGS integrated sampling devices; U.S. Geological Survey, variously dated). Replicate comparisons from the autosampler and the EWI method were similar during base-flow conditions at both stations. For stormflow at the Northeast Branch, the autosampler compared well to the EWI sampling method. Samples collected at the Northwest Branch during stormflow did not compare well because of an ephemeral side branch just above the site that contributed a lot of sand at higher velocities, and possibly because of high temporal variations in flow over the duration of sample collection. Discrete samples for SS collected on March 23, 2005 were variable between the left and right banks. Samples from the bank where the autosampler intake is located had lower total concentrations of SS and a higher percentage of finer materials: 798 mg/L and 68 percent of the material was finer than 0.63 µm in diameter. The right bank, which is below the ephemeral overflow bank (fig. 3), had 1,350 mg/L of total SS and 40 percent fine material. The sample collected from the autosampler for comparison had 670 mg/L of SS and 70 percent fine material. Differences in the time of sample collection contributed to some of the variability between these measurements, because flow in these urban streams is very flashy and variable over short time frames. During the sample collection period, flow varied from 1,470 to 1,830 ft^3/s (cubic feet per second), and a composite sample collected using the EWI method at the peak of the storm contained 2,100 mg/L of SS. Concentrations of trace metals were replicated in this example much better than the total mass of particles (average of about plus or minus 15 percent for metals as compared to plus or minus 52 percent for total SS). Most trace metals are sequestered and transported on the fine materials rather than the sand-size fractions (Horowitz, 1991).

To evaluate the recovery efficiency of the total-recoverable methods, nine samples were replicated with splits sent to the NWQL for a total-recoverable analysis and to the USGS trace-metal laboratory in Reston, Virginia for a total digestion for Zn. During base flow, sediment concentrations were low and the methods were very comparable, with Zn values all less than or equal to 5 µg/L. For stormflow samples, where there was more sediment in transport, the total digestions had concentrations that were consistently higher than those found in total-recoverable samples; the relative differences between the two methods were approximately 8 percent. This is similar to the sampling and analytical error, and although the total-recoverable metals data have a small negative bias during storms when most of the transport occurs, the fraction of metals that are unquantified is in the most refractory forms and least available to the ecosystem.

Calculation of Particulate Metal Concentrations and Enrichment Factors

To compare metal enrichments on sediments in the Anacostia River to concentrations of metals on sediments at other stations, total-recoverable trace-metal concentrations were converted to particulate concentrations by subtracting the dissolved component of the metals and normalizing to the concentration of SS. This provides the concentrations of each metal on the particles in transport (M_p in milligrams per kilogram (mg/kg), equation 1), essentially normalizing for flow. As size fractions shift during changes in flow regime, the particulate-metal concentrations may also shift. When values were censored (less than the reporting limit), they were set to zero for the purposes of this calculation. In some cases where values of dissolved metals were greater than total-recoverable because the values were small and(or) similar within analytical error, negative values were generated. These also were set to zero for the calculation. Hg was not included in this calculation because it was frequently not detected. As also had a fairly high degree of non-detects and therefore the concentrations of As should be considered a gross estimate. M_p is calculated by use of the following equation:

$$M_P = \frac{[M_{TR} - M_{dis}]}{SS} \tag{1}$$

where

M_p = Concentration of trace metals on particles in mg/kg (Concentrations of Al and Fe were converted to weight percent),

M_{TR} = Concentration of total-recoverable trace metals in µg/L,

M_{dis} = Concentration of dissolved trace metals in µg/L,

and

SS = Concentration of suspended sediment in mg/L.

Enrichment factors (EFs) of the concentrations of metals in SS in the Anacostia River over the average global crustal abundance in shales as estimated by Turekian and Wedepohl (1961) were calculated for each trace metal (equation 2). Crustal shales rather than average global crust were used for this calculation, because they approximate the fine materials in SS. For this calculation, normalization of the trace-metal concentrations to a conservative element such as Al eliminated some of the bias in the dataset due to variations in grain-size distribution and sources of rock material in the sediment (Horowitz, 1991). Ratios of enrichment may be used to infer provenance of sediment materials, and possibly contamination if the values are high enough to be significant. Because the global abundance estimates are gross averages, enrichments should be considered significant only for values that are one or more orders of magnitude higher than the crustal shales. As and Hg were not included in this analysis because the incidence of censoring in these data was too high, thus creating artifacts in the ratios. The EF is a unitless ratio.

$$EF = \frac{M_i / Al_i}{M_{ACA} / Al_{ACA}} \tag{2}$$

where

EF = Enrichment factor for the concentration of a trace metal on particulates,

M_i = Concentration of trace metal in sample,

Al_i = Concentration of Al in sample,

M_{ACA} = Concentration (abundance) of the trace metal in average crustal shale material,

and

Al_{ACA} = Concentration (abundance) of Al in average crustal shale material.

Regression Models to Predict Water Quality and Loads

Linear stepwise regression on log-transformed variables was used to develop statistical relations between continuous physical parameters and discrete sampling for the estimation of concentrations of nutrients and SS. Model development approaches followed the general procedures described in Helsel and Hirsch (1992). The first step in this analysis was to plot chemical concentrations against in-stream sensor measurements, and to visually determine if a potential relation existed. For example, a series of plots for TN, which is the sum of the concentrations of total Kjeldahl nitrogen and nitrate/nitrite, at the Northeast Branch Anacostia River station are shown in figures 8A–C. There were fairly strong and similar relations to TN for both discharge and turbidity, but they were not linear, and there was strong homoscedasticity of the residuals (the residuals were not independent of concentration). There appeared to be a subtle relation worth investigating between TN and specific conductance (SC) (fig. 8C). Values of SC originally were skewed because of road salt applied in the watershed during the winter. The increase in salinity and SC due to road salt had no relation to TN. Values influenced by road salt were basically outliers for this relation, and one solution was to remove all values over 400 µS/cm (microsiemens per centimeter), which was a road-salt threshold determined from the probability distribution of these data. The adjusted dataset for SC was tested for regression-model development.

Log transformation of these data greatly improved the linearity of the relation, but some homoscedasticity of the residuals remained (fig. 8D). Other power forms of the variables were tested, and in some cases produced better linear fits, but those model forms had unacceptable biases when the data were transformed back to real space. Without physical reasons to explain relations between the variables in other power forms, the log transforms were selected based on common usage in the literature.

The linear relation between the log-transformed values of turbidity and TN is shown in figure 8D. There is more uncertainty in this relation (coefficient of determination, R^2=0.67) than is found in the models for SS and TP, but the trend line for log-transformed data is more linear than for raw data.

After examination of the potential relations between variables, stepwise-regression models were determined using the SPlus Statistical Package, version 7.0 (Insightful Corporation). The appropriate form of each model was determined by log-transforming all the variables, starting with a formula using all variables, and then removing them one at a time, both in forward and backward steps. The final model was chosen based on several factors. The R^2 estimates the proportion of the variance in the predicted variable that is explained by the multiple independent variables in the regression equation. The estimates of R^2 should be reviewed with caution, however, because they were determined in log space and will overestimate the true variances explained by the model, once the data are transformed back into real space (McCuen, 2003). To add value to the model, the addition of a variable should substantially improve the R^2 and decrease the residual standard deviation. Other determining factors for variable inclusion in the model were regression coefficients that were sufficiently different from zero and substantially large enough to define a predictive relation, and the overall bias of the predictions based on the sum of the residuals. In some cases, the addition

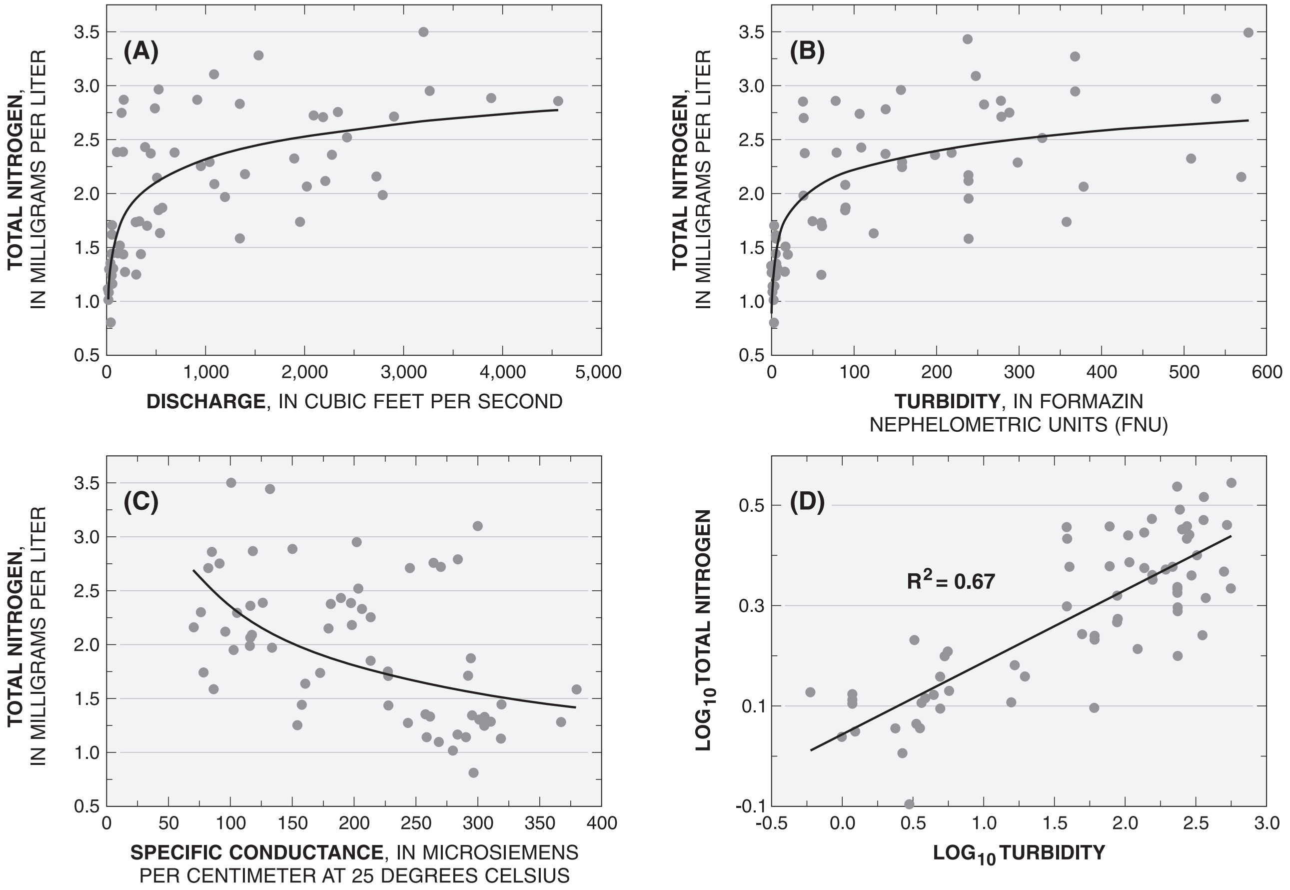

Figure 8. Total nitrogen compared to (*A*) discharge, (*B*) turbidity, and (*C*) specific conductance. (*D*) Log-transformed variables for total nitrogen compared to turbidity at the Northeast Branch Anacostia River (USGS station 01649500), 2003–05 [Outlier values of specific conductance that were influenced by road salt are removed from (*A*). Log-fitted curves are shown on figures *A* through *C*, and a linear fit with the coefficient of determination (R^2) is shown in figure *D*.]

of another variable can cause a potentially spurious coefficient to shrink, thus indicating covariance; this also was taken into consideration when refining a model.

Often, there are not clear criteria to evaluate all of the observed factors, making the selection of an appropriate model somewhat subjective. In the example for TN, the relation indicated by the correlation between $\log_{10}$SC and $\log_{10}$TN (with high values of SC filtered out) did not significantly improve the model, and the bias of the residuals was the same for both forms of the model equations. The final model determined for TN at both stations was of the form

$$\text{Log}_{10}\text{TN} \sim \beta_1 + \beta_2 \log_{10}\text{Turbidity} \qquad (3)$$

where

TN = concentration of total nitrogen in mg/L,
Turbidity is in formazin nephelometric units (FNU),
and
β_1, β_2 = regression coefficients.

The bias of each estimation was determined by transforming the estimated concentrations back to real space, plotting the residuals against the concentrations, and by calculating the actual relative bias or systematic error of the residuals (equation 4; McCuen, 2003). After transformation of the variables back into real space, the residuals were not normally distributed with higher residuals for values at higher concentrations.

$$RB_X = \frac{\bar{e}}{\bar{X}} = \frac{1}{n\bar{X}} \sum_{i=1}^{n} \hat{X}_i - X_i \qquad (4)$$

where

RB_X = the actual relative bias (bias normalized to the average concentration of a water-quality parameter),
$\bar{e}$ = the total bias or average of the residuals, predicted minus observed,

$\bar{X}$ = the average concentration of all observed measurements of the water-quality parameter,

$\hat{X}_i$ = the predicted concentration for the ith sample,

X_i = the observed concentration for the ith sample,

and

n = the number of observations or samples.

Estimates of Loads and Yields

Loads are the product of the concentration of a specific water-quality constituent and the volume flux of streamflow over a designated unit of time. For the current study, annual loads were calculated for SS, TN, and TP at each of the two Anacostia River stations for calendar years 2004 and 2005. Loads were calculated two different ways to compare (1) results from the more traditional methods that are based on a rating curve between the concentration of the parameter of interest and flow and time (Cohn, 1988; Cohn and others, 1989), and (2) estimates of concentrations from data-rich continuous in-stream measurements. Models developed in LOADEST (Runkel and others, 2004) for the current study were based on hourly time steps of flow and turbidity.

The model ESTIMATOR was developed by the USGS and employs a 7-parameter log-linear regression model with refinements to correct for bias (Cohn, 1988). In this model, measured concentrations are regressed against mean daily discharge and time, including terms for seasonality. A Minimum Variance Unbiased Estimator (MVUE) is used to correct for bias that occurs when the predicted data are transformed back from log space into real space (Bradu and Mundlak, 1970). ESTIMATOR can handle a large percentage of data below the reporting limit because it uses the Adjusted Maximum Likelihood Estimator (AMLE) to assign values of concentration to these censored data (Cohn, 1988; Cohn and others, 1992; Cohn, 2005). Multicollinearity, or non-independence between explanatory variables, is reduced or eliminated in ESTIMATOR by using centering variables. To accomplish this, the center or mean of the variable is subtracted from each occurrence and these centered variables are used in the regression (Cohn and others, 1992). ESTIMATOR is calibrated using mean daily flow, so the time step is 24 hours.

The second modeling approach used the model LOADEST, which is based on the same basic statistical design (AMLE) as the original ESTIMATOR model to provide unbiased estimates of chemical loads. The advantages of LOADEST include more flexibility to include other user-defined predictor variables such as turbidity, and smaller time steps (hourly in the current study) for short-term variability that occurs during storms and diurnal cycles. The LOADEST model may be further improved by the Least Absolute Deviation (LAD) method to correct for the non-normal distribution of the residuals using a clustering approach called “smearing” (Runkel and others, 2004). A disadvantage of the LAD method is that it would require a bootstrap simulation to calculate the standard error of the prediction (SEP), which is not practical given the size of the continuous datasets.

Uncertainties associated with each estimate of mean annual load are expressed in terms of the standard error (SE), which represents the variability that may be attributed to the parameter uncertainty. The AMLE method also calculates the SEP from which a 95-percent confidence interval for each annual-load estimate can be developed. In the current study, LOADEST and ESTIMATOR were applied and compared using the water-quality datasets from the Northeast and Northwest Branches of the Anacostia River. Loads using the LAD in LOADEST were compared to those determined with the AMLE method and were very similar (within 5 percent), so it was assumed that normality was not an important bias on the annual loads, and the AMLE loads reported herein incorporate the 95-percent confidence intervals.

A limitation on load estimates for the two Anacostia River stations is the short time span of the dataset (2 years). More accurate load estimates would require more years of data collection. Cohn (1988) recommended a minimum of 3 years of data for annual-load estimates and Yochum (2000) determined that a 9-year sliding window optimizes the regression approach used by the ESTIMATOR model. This has most likely increased the size of the confidence intervals in the current study and future modeling estimates of load and concentration would benefit from more data to refine the model.

Finally, annual load estimates were normalized to basin area to determine yields for each basin that are independent of the size of the watershed. Annual yields in kilograms per year per square kilometer for SS, TN, and TP at both of the Anacostia River stations are presented in later sections of this report.

Water Quality in the Upper Anacostia River

Two types of water-quality data were collected at the Northeast and Northwest Branches of the Anacostia River: (1) continuous measurements for discharge, pH, water temperature, SC, concentration of dissolved oxygen, and turbidity were collected from January or February 2004 through December 2005; and (2) discrete measurements of the concentrations of nutrients, SS, and trace metals were collected from July 2003 through December 2005. Hydrologic conditions in the local area during this period were average, without large extremes of wet or dry; however, the region was recovering from a severe drought that had ended the previous summer. Concentrations and loads or yields determined during the study period are assumed to be representative of average hydrologic conditions at these sites. All water-quality data are publicly available on the USGS NWISWEB website at *http://waterdata.usgs.gov/nwis*.

Flow and Physical Parameters

Data are summarized to show the median tendencies and extremes of each measurement of field conditions (table 1). Physical parameters were measured each time a discrete water-quality sample was collected and continuously with data sondes. Statistics for these data show that discrete samples were collected over a representative range of conditions at the two stations. Annual statistics for continuous-flow data may be compared to the long-term record for both stations, which extends back to 1938. Time-series plots of mean-monthly discharge with an overlay of the long-term mean-monthly discharge at each station are shown in figures 9A–B. Flow during the period of study was relatively average, but 2003 was a wetter year than 2004 or 2005 (James and others, 2003).

Median values of SC ranged from approximately 200 to 400 µS/cm. Anomalously high values of SC occurred sporadically during the winter months due to salting of roads in the watershed for deicing purposes.

Supersaturation of dissolved oxygen occurred on afternoons when biological productivity was high. The pH was in the neutral to alkaline range and also peaked each day in the afternoon during periods of increased productivity. Diurnal shifts in pH during base flow were generally up to 2 or more units of pH. These patterns in pH occurred year round, even during the winter months when biological activity is expected to be low. A multiparameter data sonde deployed in a tributary just upstream from the station at the Northeast Branch recorded even larger diurnal swings in pH, with values as high as 10 on some afternoons (fig. 10). Some of this variability can be explained by diurnal changes in productivity. No other source of alkalinity was identified upstream of these stations during the study, but the peak values of pH were higher than what might be expected based on productivity alone.

Turbidity generally was low during base-flow conditions, usually much less than 100 FNU. Maximum turbidity values occurred during storm events, and were as high as approximately 1,000 FNU. An unexplained phenomenon in turbidity was occasionally observed during base flow at both

Table 1. Statistical summaries of water chemistry at the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively)–physical parameters.

[Values presented are the median and range (in parentheses, from minimum to maximum) for the 2-year period. Measurements of physical parameters were recorded each time a water-quality sample was collected. Continuous measurements were collected in 15-minute intervals. Period of record for continuous flow data at Northeast Branch is from 1938 to the current year. Period of record for continuous flow data at Northwest Branch is from 1938 to the current year. Continuous measurements for water temperature, pH, specific conductance, turbidity, and dissolved oxygen at both stations were recorded from January 2003 through December 2005; ft^3/s, cubic feet per second; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; FNU, formazin nephelometric units; mg/L, milligrams per liter; <, less than; —, not available; Dec, December]

	Discharge, ft^3/s	pH	Water temperature, °C	Specific conductance, µS/cm at 25°C	Turbidity, FNU	Dissolved oxygen, mg/L
Northeast Branch						
Discrete data for July 2003–Dec 2005	496 (13.0–4,570)	7.2 (6.5–8.9)	12.9 (0.8–29.4)	227 (70.0–3,209)	91 (1.0–581)	10.3 (7.9–17.3)
Continuous data for water year 2004	132 (20–8,000)	7.6 (6.6–9.5)	14.0 (0.0–28.7)	362 (42–7,000)	17.9 (<1–1,000)	—
Continuous data for water year 2005	89.5 (9.4–5,130)	7.4 (6.7–9.7)	14.1 (0.0–32.0)	419 (55–6,100)	14.7 (<1–980)	11.2 (4.1–20.2)
Long-term record for 1938–2005*	175 (1.4–12,000)	—	—	—	—	—
Northwest Branch						
Discrete data for July 2003–Dec 2005	250 (6.7–3,950)	7.4 (6.3–8.3)	14.8 (0.8–26.7)	287 (75.0–2,450)	100 (<1–760)	11.0 (7.8–16.3)
Continuous data for water year 2004	80.2 (8.24–9,310)	7.4 (6.7–8.6)	17.7 (0.5–27.7)	335 (57–4,270)	21.5 (<1–850)	—
Continuous data for water year 2005	57.8 (5.1–5,000)	7.4 (6.9–9.4)	15.1 (0.0–30.5)	408 (75–6,960)	15.4 (<1–880)	10.8 (4.0–19.3)
Long-term record for 1938–2005*	49.6 (0.2–18,000)	—	—	—	—	—

* Statistics based on 1938–2005 data.

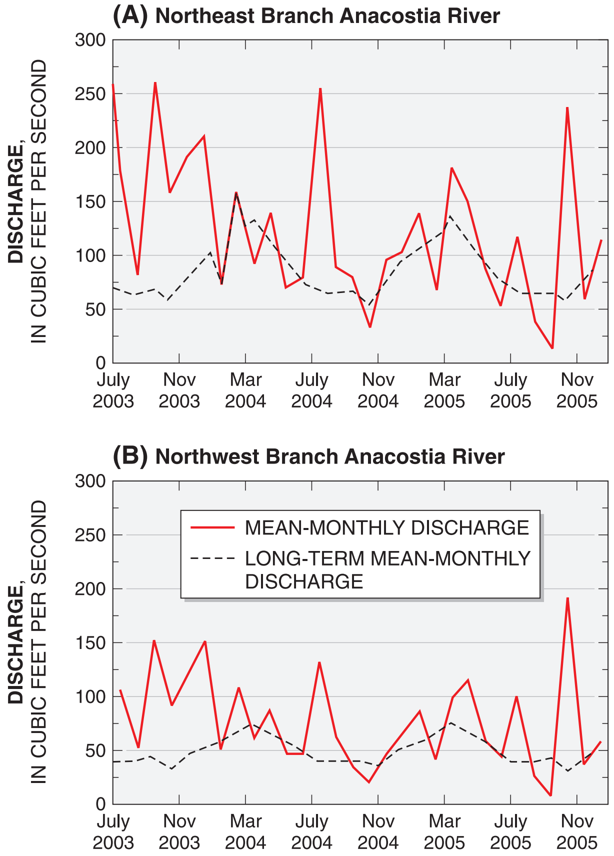

Figure 9. Mean-monthly discharge in cubic feet per second for 2003–05 compared to long-term mean-monthly discharge at the (*A*) Northeast Branch and the (*B*) Northwest Branch Anacostia River (USGS stations 01649500 and 01651000, respectively).

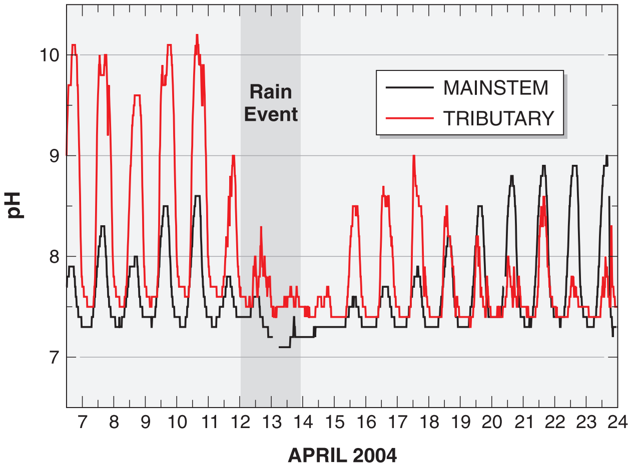

Figure 10. Diurnal variations in pH at the Northeast Branch Anacostia River at Riverdale, Maryland (USGS station 01649500), and on a small tributary that enters just above the station.

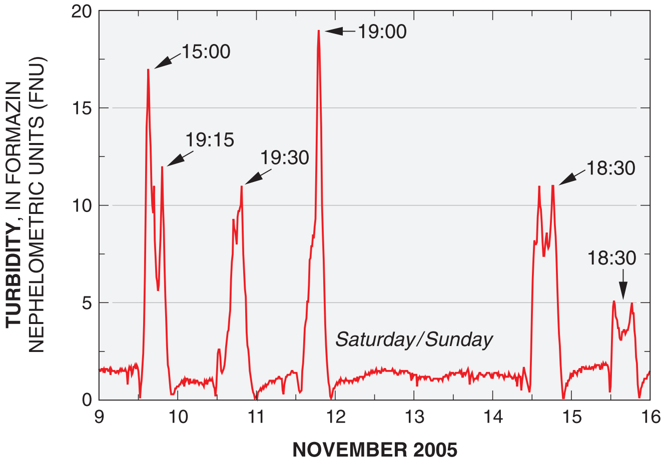

Figure 11. Short-term variations in turbidity during base flow at the Northeast Branch Anacostia River at Riverdale, Maryland (USGS station 01649500).

stations. For a short period of time, at a similar time each day, turbidity increased for several hours by about 20–30 FNU without any observed change in flow or other conditions, and then receded to previous base-flow levels. The time of day for these observations changed over the course of the study, but for the time period of each event, it was regularly observed at approximately the same time each day. An example of peaks in turbidity that occurred each day in November 2005 at approximately 19:00 Eastern Standard Time is shown in figure 11. In this example, the peaks do not occur on the weekend days (November 12 and 13), indicating that the observed peaks are related to weekday activities in the watershed. No known cause for the observed behavior was discovered during the project, but on several occasions, observations of larger changes in turbidity and SC were traced to broken sewer lines.

Nutrients, Suspended Sediment, and Total Organic Carbon

Statistical summaries of concentrations of nutrients, total organic carbon, and SS for the two Anacostia River stations are presented in table 2. Boxplots comparing the concentrations of (a) ammonia nitrogen, (b) nitrate nitrogen, (c) dissolved Kjeldahl nitrogen, (d) total Kjeldahl nitrogen, (e) total phosphorus, and (f) total organic carbon at the two Anacostia River stations and two larger integrated tributaries to Chesapeake Bay, the Susquehanna River at Conowingo, Maryland (USGS station 01578310) and the Potomac River at Washington, D.C. (USGS station 01646580) are shown in figures 12A–F. Data from the Susquehanna and Potomac Rivers were collected during the same period as part of the Chesapeake Bay River Input Monitoring (RIM) Program

Table 2. Statistical summaries of water chemistry at the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively), from July 2003 to December 2005–nutrients, total organic carbon (TOC), and suspended sediment (SS).

[Values presented are the median and range (in parentheses, from minimum to maximum) for the 2.5-year period. The complete dataset is available on the world wide web at *http://waterdata.usgs.gov/nwis*. For comparison, summaries of values for the Susquehanna and Potomac Rivers from the same period (U.S. Geological Survey, 2006) are presented; mg/L, milligrams per liter; µm, micrometers; LTMDL, long-term method detection limit; MRL, method reporting level; in some cases more than one reporting level is given because these changed over the term of the project; total nitrogen is the sum of total Kjeldahl nitrogen and nitrate/nitrite; however, values may not add up exactly to 100 percent due to rounding error; <, less than; —, not available; n, number of observations]

	Nitrate-N, mg/L	Nitrite-N, mg/L	Ammonia-N, mg/L	Ortho phosphate-P, mg/L	Soluble phosphorus, mg/L	Dissolved Kjeldahl nitrogen, mg/L	Total Kjeldahl nitrogen, mg/L	Total phosphorus, mg/L	Total nitrogen, mg/L
LTMDL	0.008	0.004/0.001	0.008/0.005	0.004/0.003	0.002	0.05	0.05	0.002	—
MRL	0.16	0.008/0.002	0.015/0.010	0.007/0.006	0.004	0.10	0.10	0.004	—
Northeast Branch (n=83)	0.75 (0.33–1.4)	0.009 (0.002–0.036)	0.074 (<0.01–0.45)	0.018 (<0.006–0.089)	0.033 (0.006–0.12)	0.51 (0.14–1.2)	1.3 (0.18–3.1)	0.25 (0.018–0.67)	2.0 (0.8–3.5)
Northwest Branch (n=81)	0.90 (0.36–2.0)	0.011 (0.003–0.08)	0.064 (<0.01–0.50)	0.12 (<0.006–0.08)	0.27 (0.002–0.11)	0.45 (0.13–2.7)	1.6 (0.16–5.1)	0.33 (0.010–0.93)	2.4 (0.91–5.9)
Susquehanna River (n=45)	1.3 (0.72–2.1)	0.009 (0.004–0.14)	0.04 (<0.04–0.16)	0.0075 (<0.006–0.08)	0.011 (<0.01–0.1)	0.24 (0.12–0.69)	0.34 (0.19–0.89)	0.05 (0.015–0.23)	1.6 (1.1–3.1)
Potomac River (n=62)	1.3 (0.53–2.1)	0.008 (<0.008–0.16)	<0.04 (<0.04–0.08)	0.012 (<0.006–0.11)	0.024 (<0.01–0.13)	0.21 (0.11–0.48)	0.47 (0.16–2.2)	0.051 (0.007–0.70)	2.0 (1.4–3.5)

	Total organic carbon, mg/L	Suspended sediment, mg/L	Percent of sediment finer than 0.63 µm
LTMDL	0.2	—	—
MRL	0.4	1	—
Northeast Branch (n=83)	4.8 (1.8–24)	180 (1–1,975)	73 (36–95)
Northwest Branch (n=81)	4.8 (1.4–19)	373 (2–1,700)	77 (43–94)
Susquehanna River (n=45)	3.1 (1.9–11)	14 (2–173)	—
Potomac River (n=62)	5.2 (2.2–26)	14 (1–788)	—

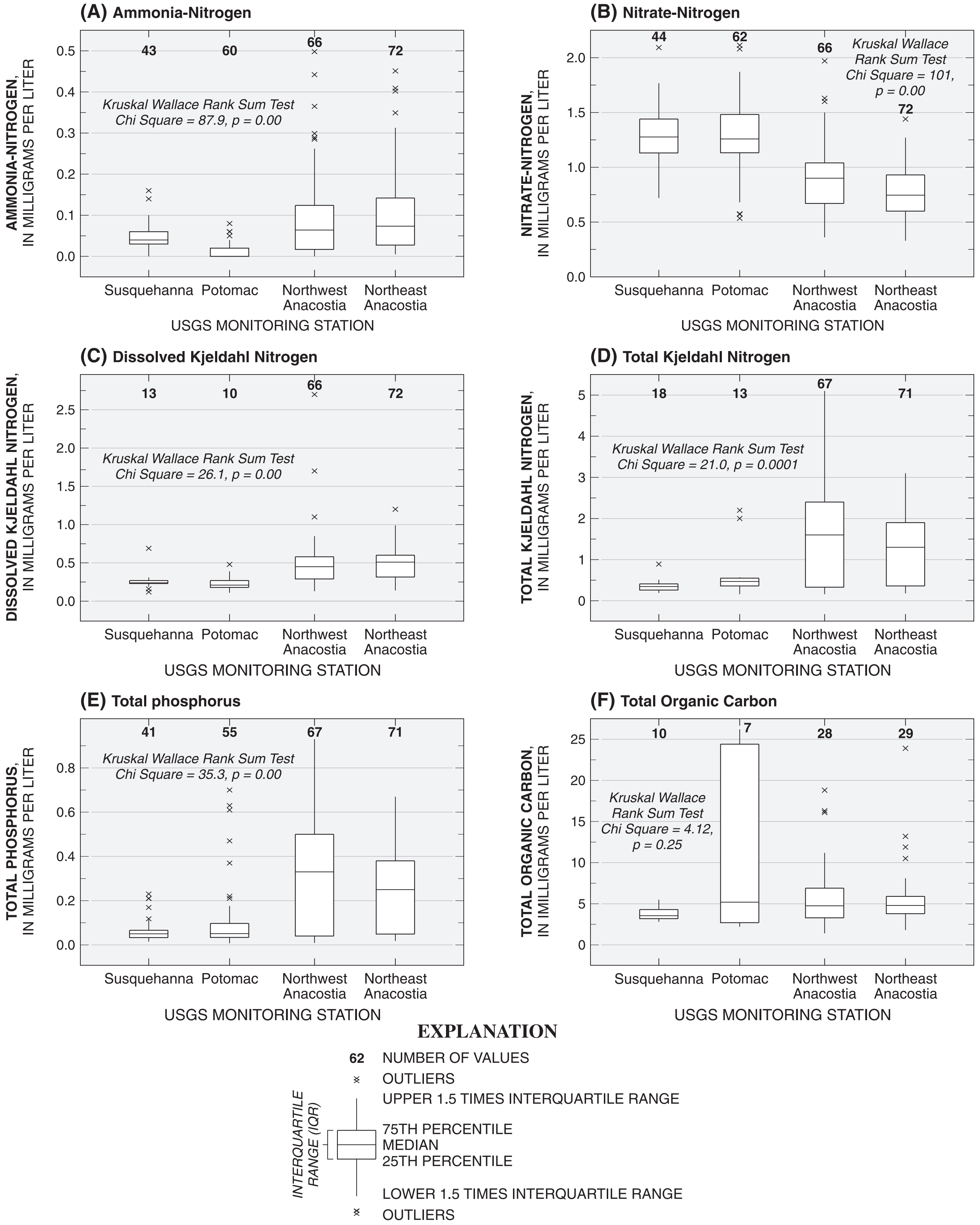

Figure 12. Boxplots comparing concentrations of selected parameters between the Northwest Branch and Northeast Branch Anacostia River (USGS stations 01651000 and 01649500, respectively), the Susquehanna River (USGS station 01578310), and the Potomac River (USGS station 01646580). The data were collected during the same time period, and both studies emphasized storm sampling.

(U.S. Geological Survey, 2006). Although there were no statistically significant differences in the concentrations of SS and nutrients between the two Anacostia River sites (table 2), the concentrations at both of these stations differ from those at the RIM sites. Differences in the median concentrations of ammonia, nitrate, total Kjeldahl nitrogen, and total phosphorus among the four basins were determined by the Kruskal Wallis Rank Sum test and were significant for each set of boxplots (figs. 12A–E). Differences in the median concentrations of total organic carbon were not significant between sites (fig. 12F). Chi square and p values for the comparisons are reported with each plot.

There are basic differences in nutrient chemistry in small urban streams as compared to larger river systems with a majority of agricultural, forested, or more integrated land use in their basins. For example, nitrate is typically the dominant form of nitrogen in many streams. Maximum concentrations of nitrate in streams commonly occur during base flow when ground water is the major component of flow, and are lower during storms, when the stream is diluted by rain and surface runoff. Time-series plots of the concentrations of nitrogen species in figure 13A demonstrate this typical behavior for the Susquehanna River, where the dominant form of nitrogen consistently was nitrate. Concentrations of nutrients in the Potomac River at Chain Bridge in Washington, D.C. are not plotted here, but were similar. The same major species of nitrogen plotted over time for the Anacostia River stations (figs. 13B–C) showed a very different pattern that probably is more typical of small urban streams. At these stations, the dominant form of nitrogen was organic particles that were transported mainly during storm events. Ammonia was a small component of total nitrogen in all the rivers, but in the urban settings, ammonia was almost always present and the concentrations increased slightly rather than being diluted during storm events. A major source of ammonia in the Anacostia River is likely the degradation of organic matter. It has not been determined what portion of organic matter was stored in bed sediment that was resuspended during storm events, and how much was washed in from the watershed. Both dissolved and total Kjeldahl nitrogen consistently increased during storm events, and it is likely that a mixture of sources of organic nitrogen were responsible.

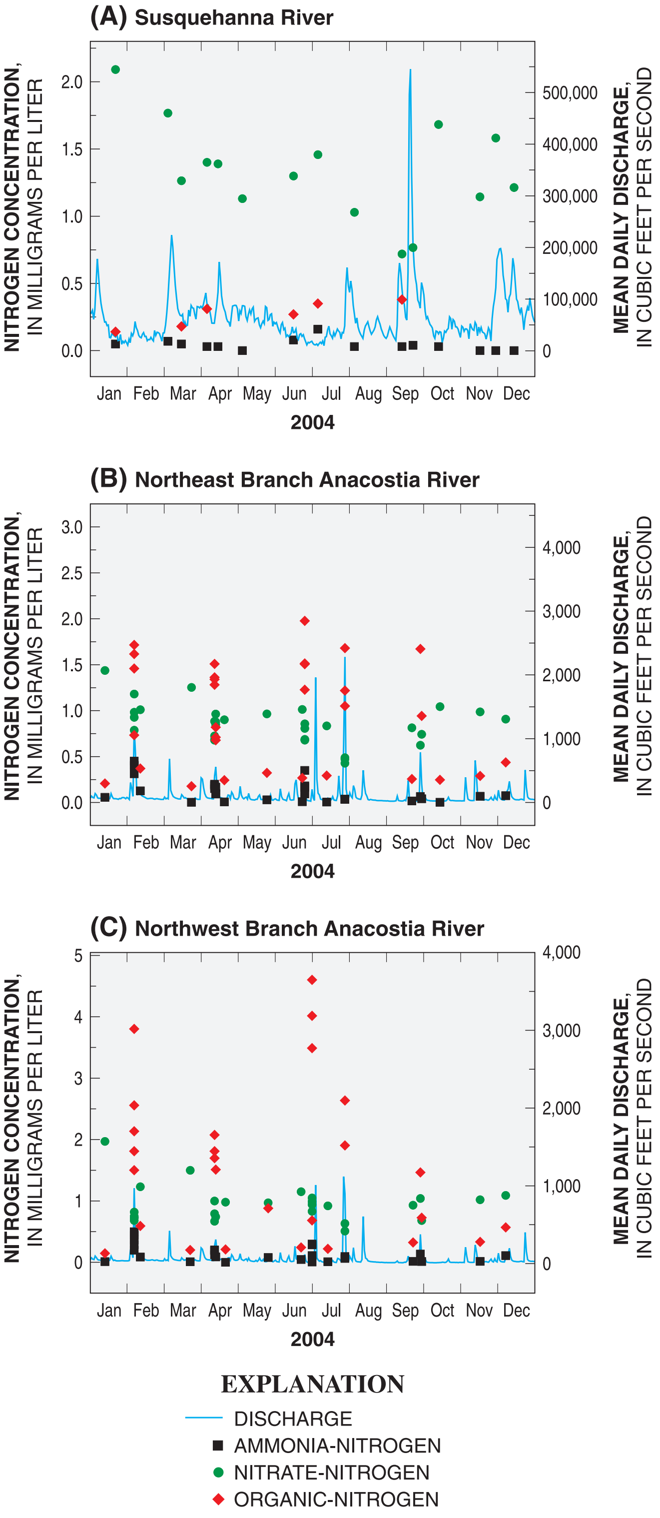

Figure 13. Major species of nitrogen and mean daily discharge in 2004 and 2005 at the (*A*) Susquehanna River at Conowingo, Maryland (USGS station 01578310), (*B*) Northeast Branch Anacostia River (USGS station 01649500), and (*C*) Northwest Branch Anacostia River (USGS station 01651000). [Scales vary on y-axes in each plot.]

Trace Metals

Concentrations of trace metals are summarized in table 3. For comparison, ranges of concentrations from other regional and national studies are provided. Concentrations from the USGS Fall Line Toxics Program (Chesapeake Bay Program, 1996) are from two base-flow synoptic surveys (fall and spring 1994) at the limits of tidal effects in nine major tributaries of the Chesapeake Bay, and a fixed-station study from 1990–93 on the Susquehanna River (USGS Station 01578310). Methods used for the Fall Line Toxics Program were generally the same as those used in the current study except that detection limits

Table 3. Statistical summaries of water chemistry at the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively) from July 2003 to December 2005–trace metals.

[Values presented are the median and the range (in parentheses, from minimum to maximum) for the 2-year period. The complete dataset is available on the world wide web at *http://waterdata.usgs.gov/nwis*. Concentration data from other studies are included for comparison: Chesapeake Bay synoptic summaries of nine major tributaries sampled twice during 1994 (Chesapeake Bay Program, 1996)[a]; dissolved and total-recoverable metal concentrations measured in the Susquehanna River from 1990–93 by the USGS Fall Line Toxics Program (data available on request from USGS MD-DE-DC WSC)[b]; typical metal concentration in streams from Drever (1999)[c]; ranges of concentrations of trace metals in river and basin bed sediment in the tidal Anacostia River, Washington, D.C. (Velinsky and others, 1994)[d]; crustal abundances of the elements in average shales from Turekian and Wedepohl (1961)[e]; and ranges of particulate metal concentrations from National Water-Quality Assessment (NAWQA) Program data summaries for sieved bed sediment (<0.63 μm fraction) from Rice (1999)[f]; summaries of metal concentrations in urban lake sediments from Mahler and others (2006)[g]; units for dissolved and total-recoverable metals are in micrograms per liter (μg/L); units for particulate metal concentrations are in milligrams per kilogram (mg/kg) of dry weight of the suspended particles, except that aluminum and iron are presented in mass percent; LTMDL, long-term method detection limit; MRL, method reporting level; E, value is greater than the LTMDL but less than the MRL and is coded as estimated because of lower precision in this value; <, less than; —, not available]

	Aluminum	Arsenic	Cadmium	Chromium	Cobalt	Copper
Dissolved concentrations						
LTMDL	*0.8*	*0.1*	*0.018*	*0.4/0.02*	*0.02*	*0.2*
MRL	*1.6*	*0.2*	*0.04*	*0.8/0.04*	*0.04*	*0.4*
Northeast Branch	32 (3.6–380)	0.55 (<0.2–1.1)	0.043 (<0.04–0.29)	E0.73 (<0.8–9.4)	1.2 (0.15–4.3)	3.9 (1.1–8.2)
Northwest Branch	21 (4.1–220)	0.46 (<0.2–2.7)	E0.033 (<0.04–0.38)	0.55 (<0.8–2.7)	0.48 (0.07–1.4)	3.6 (0.44–7.1)
Fall Line tributaries (1994)[a]	*8.4–115*	*0.08–0.47*	*0.01–0.24*	*0.03–0.28*	—	*0.11–2.3*
Susquehanna River 1990–93[b]	30 (<10–230)	<1 (<0.6–1.2)	<1 (<1–1.2)	<1 (<0.2–5.4)	<3	2 (<1–8)
Typical Stream[c]	*50*	*2*	—	*1*	*0.2*	*7*
Total-recoverable concentrations						
LTMDL	*1*	*0.9/0.06*	*0.018*	*0.4/0.02*	*0.02*	*0.3*
MRL	*2*	*1.9/0.12*	*0.04*	*0.8/0.04*	*0.04*	*0.6*
Northeast Branch	960 (27–11,000)	E1.4 (E0.22–3.5)	0.16 (<0.04–0.55)	8.6 (0.54–28)	5.0 (0.43–28)	13 (1.5–40)
Northwest Branch	3,700 (41–13,000)	E1.4 (E0.18–5.7)	0.16 (0.02–1.4)	10 (<0.8–33)	6.7 (0.66–24)	19 (1.3–85)
Susquehanna River 1990–93[b]	—	<1 (<1–1)	<1 (<1–1)	2 (<1–10)	—	3 (<1–11)
Particulate concentrations						
Northeast Branch	0.63 (0.17–3.7)	1.3 (<1–89)	0.50 (<1–13)	34 (<1–600)	18 (<1–129)	35 (<1–200)
Northwest Branch	1.0 (0.49–4.6)	0.63 (<1–270)	0.48 (<1–8.3)	25 (<1–250)	16 (<1–205)	50 (<1–400)
Fall Line tributaries (1994)[a]	*0.09–17.9*	—	*0.52–33*	*20–320*	—	*2.6–281*
Tidal Anacostia[d]	—	—	*0.45–3.2*	*51-155*	—	*33–126*
Crustal Abundance (Shale)[e]	*8.0*	*13*	*0.3*	*90*	*19*	*45*
NAWQA[f]	*6.4 (1.4–14)*	*6.3 (1–200)*	*0.4 (<0.1–56)*	*64 (<1–700)*	—	*27 (6–620)*
NAWQA (Lake sediments, 1990s: dense urban/light urban/reference)[g]	—	—	*1.60/0.49/0.64*	*75/65/47*	—	*83/68/34*

Table 3. Statistical summaries of water chemistry at the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively) from July 2003 to December 2005–trace metals.—Continued

Iron	**Lead**	**Manganese**	**Mercury**	**Nickel**	**Zinc**	
		Dissolved concentrations				
1	*0.04*	*0.1*	*0.009*	*0.03*	*0.3*	*LTMDL*
2	*0.08*	*0.2*	*0.02*	*0.06*	*0.6*	*MRL*
190 (51–480)	0.46 (0.067–1.7)	59 (1.8–230)	<0.02	4.0 (1.9–6.5)	12 (1.6–55)	**Northeast Branch**
135 (<0.6–467)	0.35 (E0.046–1.8)	60 (2.3–197)	<0.02	2.7 (0.66–4.5)	6.1 (1.5–29)	**Northwest Branch**
21–1,495	*<0.03–0.39*	*1.4–135*	*<0.1*	*<0.1–3.2*	*0.3–19*	*Fall Line tributaries (1994)*[a]
21.5 (<3–810)	<1 (<0.06–5)	40 (2.0–170)	0.021 (<0.1–0.20)	3 (<1–9)	1.6 (<3–22)	*Susquehanna River 1990–93*[b]
40	*1*	*8*	*0.07*	*2*	*30*	*Typical Stream*[c]
		Total-recoverable concentrations				
3/1	*0.1*	*0.3*	*0.005*	*0.08*	*1.0*	*LTMDL*
6/2	*0.2*	*0.6*	*0.018*	*0.16*	*2.0*	*MRL*
3,050 (30–20,000)	14 (0.36–57)	200 (25–1,500)	0.026 (<0.018–0.11)	9.8 (2.8–42)	68 (2.9–460)	**Northeast Branch**
5,900 (360–22,000)	20 (E0.12–150)	430 (52–1,900)	0.039 (<0.018–0.14)	14 (2.4–58)	70 (3.0–380)	**Northwest Branch**
640 (160–3,000)	2 (<1–17)	120 (25–190)	<0.1 (<0.1–1)	5.5 (2.0–23)	10 (<10–50)	*Susquehanna River 1990–93*[b]
		Particulate concentrations				
1.8 (0.27–24)	79 (14–203)	560 (<1–5,600)	—	24 (<1–205)	260 (<1–3,900)	**Northeast Branch**
1.9 (0.94–12)	64 (20–440)	940 (<1–22,000)	—	35 (<1–580)	200 (<1–1,900)	**Northwest Branch**
0.02–18.4	*<3.0–130*	*29–16,830*	—	*0.7–331*	*<3.0–1,095*	*Fall Line tributaries (1994)*[a]
—	*32–409*	—	*0.2–1.0*	—	*137–512*	*Tidal Anacostia*[d]
4.7	*20*	*850*	*0.4*	*68*	*95*	*Crustal Abundance (Shale)*[e]
3.5 *(0.7–19)*	*27* *(<0.7–19)*	—	—	*27* *(6–530)*	*110* *(<4–9,000)*	*NAWQA*[f]
—	*214/56/48*	—	—	—	*343/203/134*	*NAWQA (Lake sediments, 1990s: dense urban/light urban/reference)*[g]

and analytical precision have improved since the early 1990s. Typical stream values for dissolved metals in the United States are presented from Drever (1999).

Dissolved concentrations for metals sampled in the Anacostia River were similar between the two Anacostia River stations and to those in the Susquehanna River and in other streams across the United States. This indicates that the concentrations of dissolved trace metals in these typical urban streams may be controlled by solubility, and are probably more regulated by physical parameters such as temperature, pH, and redox than by variations in sources and hydrology.

Concentrations of dissolved trace metals at the Anacostia River stations were compared to guidelines and criteria established by the U.S. Environmental Protection Agency (USEPA) (2006) and the Canadian Council of Ministers of the Environment (CCME) (2006) for the protection of aquatic life in freshwater (Appendix). The toxicity of most of these metals is a function of hardness and(or) alkalinity, which were not determined during the current study, so comparisons are made relative to a general description of water quality and should be considered with caution. In some instances, dissolved concentrations of Cd, Pb, Cu, Ni, and(or) Zn exceeded the CCME guidelines, which are the more stringent of the two, but with the exception of a few values of dissolved Cd at both stations that were just above chronic levels, most values did not exceed the USEPA criteria.

A positive correlation was found between the dissolved concentrations of three trace metals: Mn, Co, and Ni. This is a natural geochemical association found commonly in a number of environmental settings and may be compared to redox processes that form Mn nodules on the ocean floor (Burdige, 1993). The correlation is not likely to be directly related to urban processes, but may be indirectly related to periodic anoxic conditions in bed sediment.

Total-recoverable metals in the Anacostia River, except for Cd, had concentrations that were significantly higher than those found in the Susquehanna River (Chesapeake Bay Program, 1996) (table 3; $p < 0.05$ for the Kruskal Wallis Rank Sum Test). Total-recoverable metals include metals that are transported in the particulate fraction, where metals naturally partition, so they are good indicators of the total metal load in each river.

To facilitate comparison of metal enrichments on sediment in the Anacostia River to sediment from other stations, concentrations of total-recoverable trace metals were converted to particulate concentrations (equation 1; table 3). Calculated concentrations of particulate metals were compared to estimates of their global crustal abundance in average shale materials (Turekian and Wedepohl, 1961) and to two national summaries (samples collected across the conterminous United States) from the USGS National Water-Quality Assessment (NAWQA) Program. NAWQA summarized results of metal concentrations on streambed sediments (Rice, 1999) and in urban-lake bed sediments (Mahler and others, 2006). Three different values for the median concentrations in recent (1990) lake-bed sediments are shown from the study by Mahler and others in table 3: dense urban (greater than 52 percent urban land use in the watershed), light urban (6–43 percent urban land use), and reference (less than 1.5 percent urban land use). The concentrations of metals associated with SS at both Anacostia River stations are highly variable, but median values are similar to crustal shales and fall in the range of other light urban streams. Particulate concentrations also compared well to values measured during 1995–96 on the Anacostia River by Gruessner and others (1997), although the total suspended solids observed in that study were much lower than totals found during most of the storms in the current study.

Metal Enrichment Factors

Enrichment factors over the global crustal abundance in shales were calculated for each trace metal (equation 2). These factors are ratios that normalize the observed concentrations of metals on SS in the Anacostia River to average baseline concentrations in crustal shales. Boxplots comparing the statistical distributions of the calculated EFs for each trace metal at the two Anacostia River stations are shown in figures 14A–B. For all of the metals in this analysis, there appears to be some enrichment over the concentrations in average shales, but most of the EFs were substantially lower than a factor of 100, and the median factors were usually less than 10. The median EFs for Cr, Co, Cu, and Ni appeared to be very close to unity with the exception of some outliers in the datasets. Values for Cd, Pb, and Zn were higher than those found for the other metals, and may be related to urban sources; however, these values are not large enough to define major enrichments or to provide evidence of significant local sources of contamination. Results of the EF calculations confirm the earlier comparison to the national dataset of Mahler and others (2006)—that the upper watershed of the Anacostia River falls into the category of light urban land use.

Hydrologic and Seasonal Effects on Water Quality

For many of the metals, higher particulate concentrations were found during base flow as compared to the metals on SS in transport during storm events. The median values of the calculated particulate-metal concentrations and EFs grouped according to flow for the two Anacostia River stations are shown in table 4. Again, As and Hg were not included in this analysis because of the high rate of censoring in these data. The appropriate cutoffs between base flow and stormflow were determined using probability plots of the distributions of discharge, and found to be at approximately 100 ft^3/s at both sites. Flow greater than 100 ft^3/s includes all instances of excess flow, including high base flow. When differences were significant, as determined with a Wilcoxon Rank Sum Test ($p < 0.05$), the cells in table 4 are shaded and bolded.

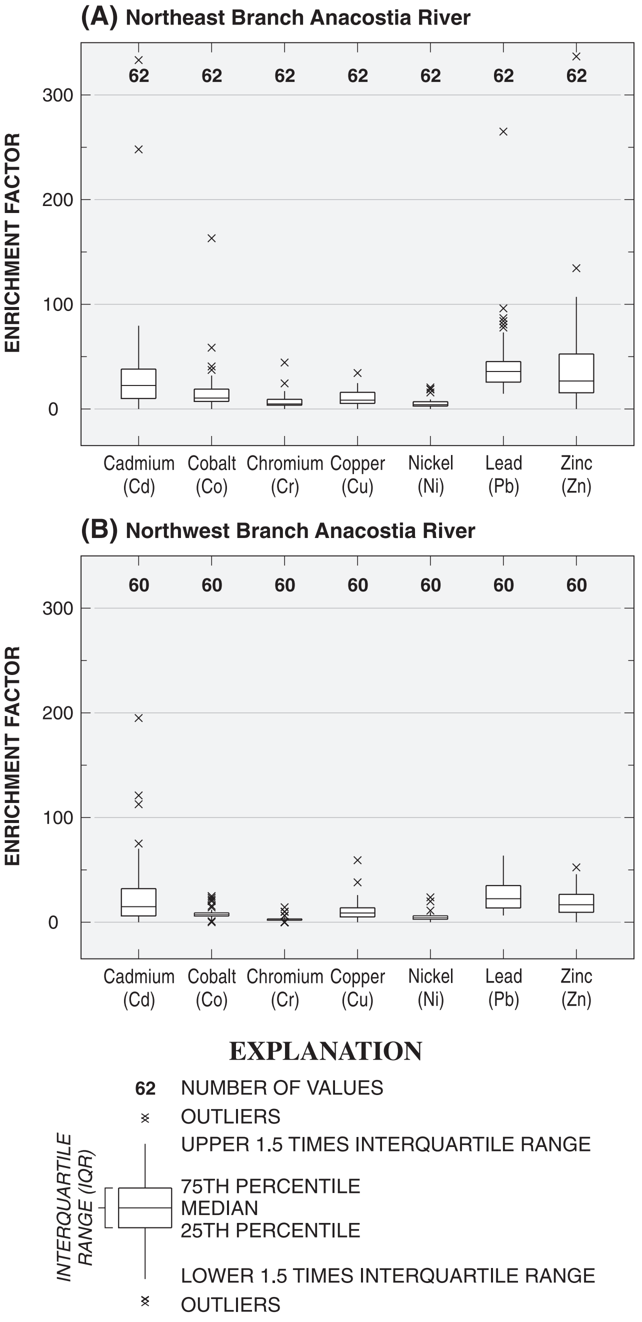

Figure 14. Statistical distributions of enrichment factors (EF) for trace metals at (*A*) Northeast Branch, and (*B*) Northwest Branch Anacostia River (USGS stations 01649500 and 01651000, respectively). [EF are unitless ratios.]

A likely explanation for the observed differences is that the size of the particles changes during different flow regimes, with coarser sand-size particles being mobilized during higher-energy events. When the same analysis was done on the EFs (table 4), differences between the two flow regimes were smaller and less often significant, supporting the observation that the shift in particulate concentrations is related to variations in particle size rather than a shift in sources of sediment that have different enrichments. As was found for nitrogen and phosphorus, metals are transported mainly on particulate phases, particularly in the smaller size fractions due to their higher surface areas, more charged surfaces, and better scavenging potentials (Horowitz, 1991).

To test for seasonal or other time-related variability in water quality, selected parameters were plotted with groupings by month (figs. 15A–C). Boxplots are presented for (a) TN, (b) TP, and (c) total-recoverable Zn, and values that are plotted are total recoverable in whole-water concentrations rather than particulate. In all three cases (figs. 15A–C), the differences between months were not large, but did show a relation to flow, with the highest concentrations occurring during months with high flows. Because many of the water-quality parameters that were measured are very strongly particle-reactive, their volume-based concentrations (in micrograms per liter) increased during storm events when flows were greater and more SS was in transport. This is in contrast to the mass-based particulate concentrations (in milligrams per kilogram), which generally decrease during the course of a storm as more sand-size particles are transported.

Velinsky and others (1994) compared metals in SS and bed sediment in the tidal Anacostia River Basin to metals in sediment at outfalls and in sewers. They concluded that the major sources of trace metals, particularly Pb, were local for the tidal reaches, coming from both stormwater and the combined sewer systems. They calculated EFs for river and basin bed sediment using different normalization calculations than those used during the current study, normalizing to Fe and to average concentrations in the Chesapeake Bay drainage area, which they assumed to be “unimpacted” local sediment. Results of their enrichment calculations, however, were similar to those found in SS at the Northeast and Northwest Branches by the current study, indicating possibly similar sources and loads for metals in both the tidal and nontidal reaches of the Anacostia River.

In a later study, Velinsky and others (1999) found consistently higher concentrations of both dissolved and total-recoverable trace metals at the Northeast Branch station than at the Northwest Branch station. Comparisons of results from both of these stations and the lower tidal stations were variable, but Velinsky and others (1999) concluded that there was a significant flux of trace metals and nutrients from the nontidal watershed to the upper tidal waters. In the current study, concentrations of dissolved and total-recoverable metals were similar between the Northwest and Northeast Branch stations.

Table 4. Median values for concentrations of metals on particulates and enrichment factors for the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively) for data collected from July 2003 through December 2005, grouped by flow regime.

[Values that are significantly different for base flow compared to flow greater than 100 cubic feet per second (ft^3/s) are in **bold** with a shaded cell ($p < 0.05$ for the Wilcoxon Rank Sum Test); <, greater than; ft^3/s, cubic feet per second; µg/L, micrograms per liter]

	Northeast Branch				Northwest Branch			
	Particulate metal concentration, µg/L		Enrichment factor, unitless		Particulate metal concentration, µg/L		Enrichment factor, unitless	
	Base flow	Flow > 100 ft^3/s	Base flow	Flow > 100 ft^3/s	Base flow	Flow > 100 ft^3/s	Base flow	Flow > 100 ft^3/s
Cadmium	0.6	0.5	15	23	0.9	0.5	16	14
Chromium	**140**	**27**	**10**	**4**	48	23	3	2
Cobalt	22	18	**7**	**12**	**25**	**15**	8	7
Copper	**67**	**30**	9	8	**100**	**39**	**13**	**8**
Lead	**97**	**53**	27	38	71	62	16	28
Nickel	20	24	**2**	**4**	**60**	**32**	5	4
Zinc	**420**	**220**	25	27	**320**	**170**	19	16

Anatomy of a Storm—Patterns of Water Quality

One way to better understand the dynamics of contaminant transport behavior in surface water is to examine the shifts in physical and chemical parameters over the course of one or more individual storm events. The use of an autosampler enabled this analysis with the collection of multiple discrete samples of water quality over storm hydrographs. These samples, combined with continuous water-quality monitoring data, provide some insight into the transport processes that occur during storm events. Several storms that occurred in March and April 2005 on the Northeast Branch of the Anacostia River were used for this analysis.

Time-series plots of physical parameters (fig. 16) measured in the river over the three storms followed predictable patterns. Stream discharge was flashy; the stream increased in response to precipitation within 1 to 3 hours of the onset of each storm. Discharge increased quickly, reached peak flow, and started to recede within about 12 hours after the end of each rainfall event. The hydrograph showed multiple peaks and plateaus as rainfall intensity shifted up and down, as different parts of the upstream watershed responded to the storm, and as the ground-water component of flow increased from recharge to the shallow water table. Rapid response is typical of urban streams where the channels have been straightened and stabilized with riprap and where impervious surfaces retard shallow infiltration of recharge to ground water.

As rainfall diluted the water in stream base flow, chemical and physical parameters shifted accordingly (fig. 16). Temperature decreased slightly, and SC decreased as cooler low-ionic-strength rainwater entered the stream. The diurnal patterns in pH and dissolved oxygen that are produced by biological productivity and respiration during base-flow conditions were dampened during each storm. Rainwater is not strongly buffered, but large volumes, combined with increasing turbulence in the stream, temporarily overshadowed the biological processes and the background alkalinity of the stream. Similarly, the concentration of dissolved oxygen was closer to equilibrium with the atmosphere from the addition of rainwater and from increased reaeration with turbulent flow.

The relation of turbidity to flow was closely correlated, but was hysteretic, with peaks for discharge and turbidity occurring at different times during the events. There are a number of processes that contribute to the suspension and mobility of sediment during a storm event. First, there is an initial flush from overland flow that washes sediment into the stream, and an initial surge in energy within the stream that mobilizes flocculent (fine-grained) and loosely held sediment from the streambed. As energy in the stream increases, coarser material is brought into transport, and at the peak of a storm hydrograph, sand-size material becomes an important component of the suspended load. This was often observed in the water-quality data during storms, as increases in the concentration of total SS early in the storm hydrographs, and decreases in the percent of sediment finer than 0.63 µm as the storms progressed.

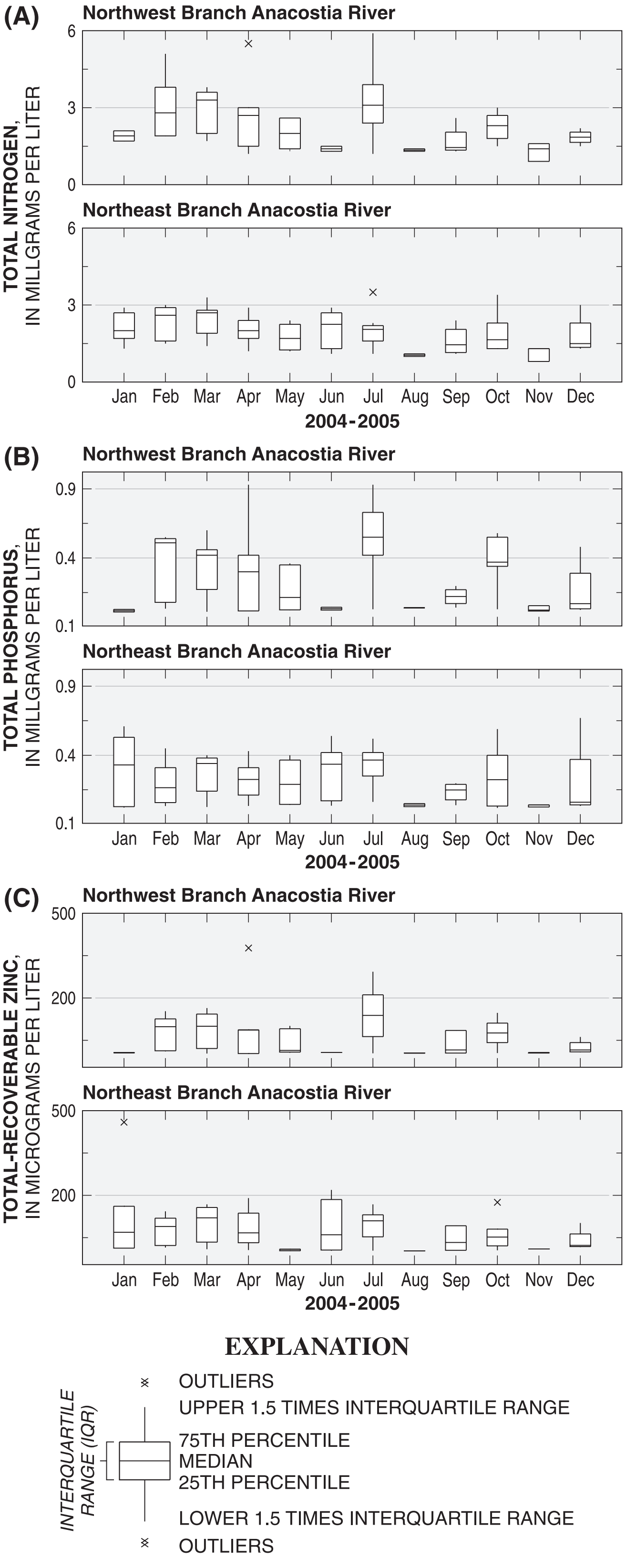

Figure 15. Monthly variations in the concentrations of (*A*) total nitrogen, (*B*) total phosphorus, and (*C*) total-recoverable zinc. [Data are grouped by month and cover the period of 2004–05]

A time-series plot of the concentration of suspended sediment over the first March storm in 2005 on the Northeast Branch Anacostia River is shown in figure 17 and demonstrates the early flush or resuspension of sediment. A sample was not collected immediately preceding the storm, but a base-flow sample was collected about 2 weeks prior to the storm; the concentrations of SS and other parameters in that sample are shown on this and subsequent plots for reference. A second peak in SS occurred as discharge neared its peak and was likely related to increases in the transport of sand at the highest stream velocities. The fraction of sediment finer than 0.63 μm dropped to 52 percent at the peak of the storm; average base-flow fractions of fine sediment were approximately 90 percent.

The understanding of physical processes in the stream forms a basis for interpretation of the water and sediment chemistry. A time-series plot of the concentrations of nitrogen species over the first March storm in 2005 is shown in figure 18. As already noted, the major portion of nitrogen in these two urban streams was transported as particulate organic nitrogen. As was the case with SS, the curve of total Kjeldahl nitrogen increased sharply at the beginning of the storm and peaked early, well before the final peak of flow. There was no second nitrogen peak as found with SS, because sand particles are chemically cleaner as compared to finer particles and, as previously discussed, sand becomes an important component of the sediment at high-flow velocities. Ammonia nitrogen also increased slightly at the onset of the storm and then slowly receded as the storm progressed. Nitrate and nitrite forms of nitrogen decreased slightly during the storm and increased slowly again towards the end when ground water from base flow and interflow were reestablished as a large component of flow. The dilution effect on nitrate-nitrogen was much less pronounced than in other streams such as the Susquehanna River, however (fig. 13).

The concentration of TP behaved predictably during storm events, being influenced by the transport of SS (fig. 19). TP increased quickly at the onset of the storm, peaking well before the peak in flow, likely on a combination of the first flush of runoff and disturbance of the more flocculent (fine-grained) bed sediment. TP remained high during the storm, and after flow had peaked, did not decrease until well into the receding limb of the storm. Conversely, dissolved phosphorus behaved similarly to nitrate/nitrite, showing a slight dilution effect during the storm that recovered as flow ebbed.

The concentrations of total-recoverable and dissolved trace metals during the storm events were plotted with the particulate concentrations and EFs. The different phases of Zn, Pb, Cu, and Cr are shown in figures 20A–D, respectively. Zn is an insoluble and strongly particle-reactive trace metal. Concentrations of total-recoverable Zn (fig. 20A) increased quickly at the onset of the storm, and then slowly started to decline even before the peak of the hydrograph, as the size fractions of the sediment shifted toward coarser particles. Total-recoverable Zn continued to decline as the storm ebbed, until it returned to base-flow concentrations. By calculation,

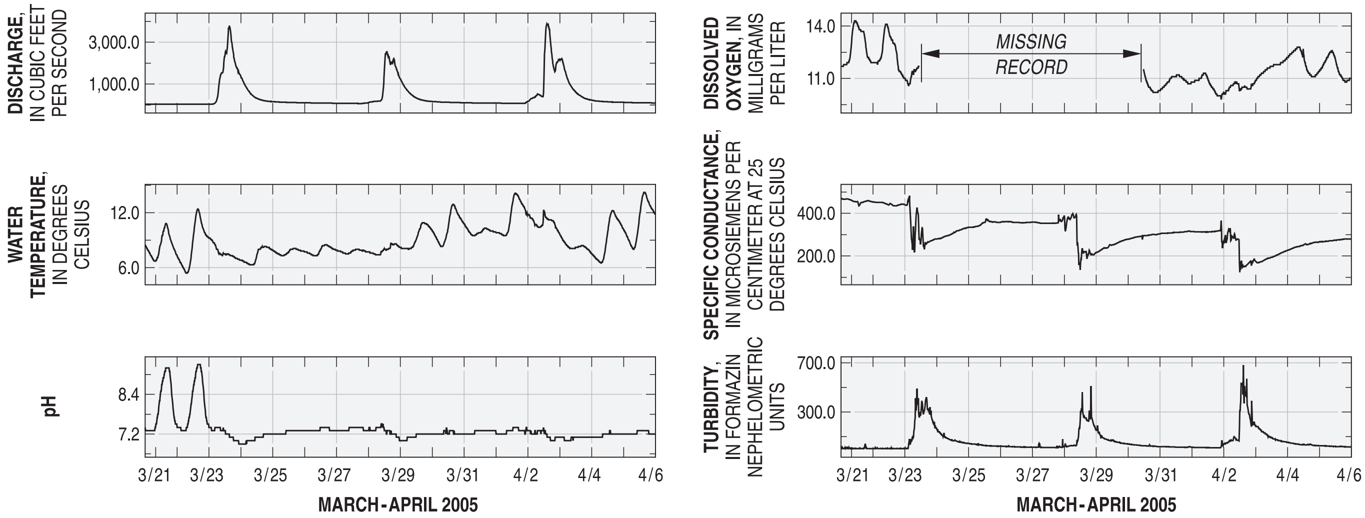

Figure 16. Physical parameters—discharge, water temperature, pH, concentration of dissolved oxygen, specific conductance, and turbidity for a series of storms in March and April 2005 on the Northeast Branch Anacostia River (USGS station 01649500).

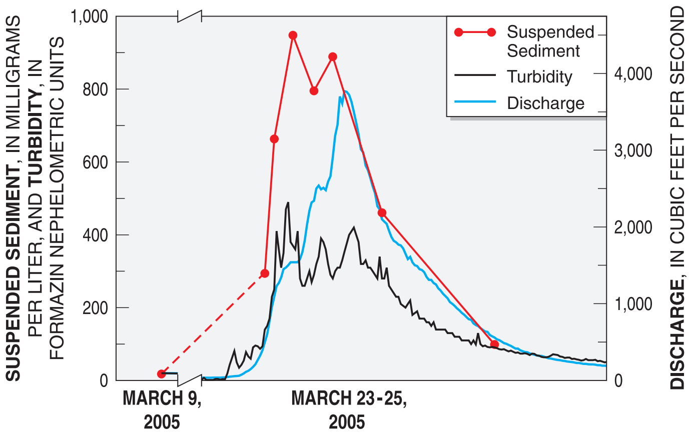

Figure 17. Discharge, turbidity, and concentration of suspended sediment during a storm in March 2005 on the Northeast Branch Anacostia River (USGS station 01649500). [X-axis is broken during the 2-week period between the base-flow sample on March 9 and the storm event of March 23–25, 2005.]

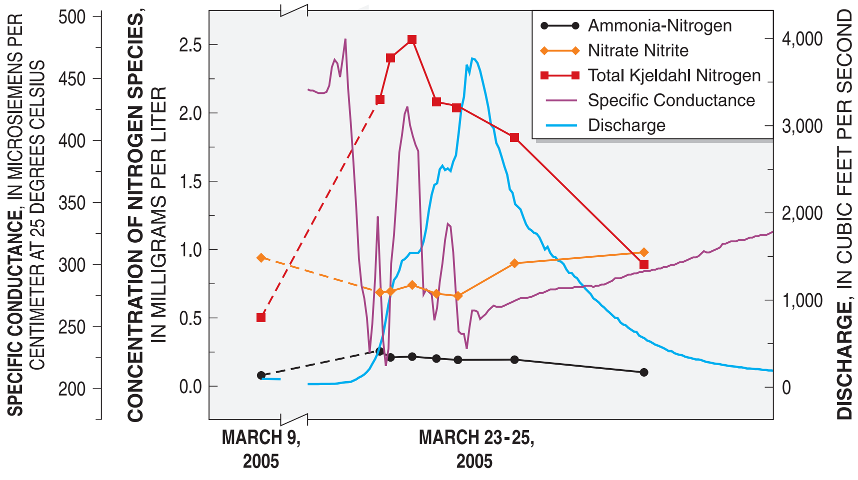

Figure 18. Discharge, specific conductance, and concentrations of nitrogen species during a storm in March 2005 on the Northeast Branch Anacostia River (USGS station 01649500). [X-axis is broken during the 2-week period between the base-flow sample on March 9 and the storm event of March 23–25, 2005.]

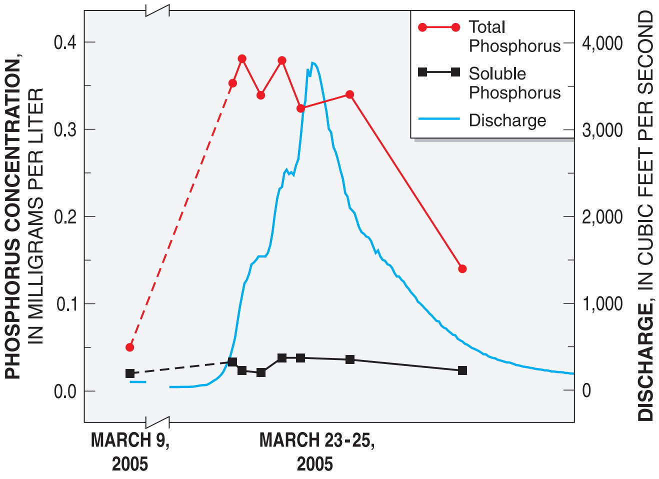

Figure 19. Discharge and concentrations of total and dissolved phosphorus during a storm in March 2005 on the Northeast Branch Anacostia River (USGS station 01649500). [X-axis is broken during the 2-week period between the base-flow sample on March 9 and the storm event of March 23–25, 2005.]

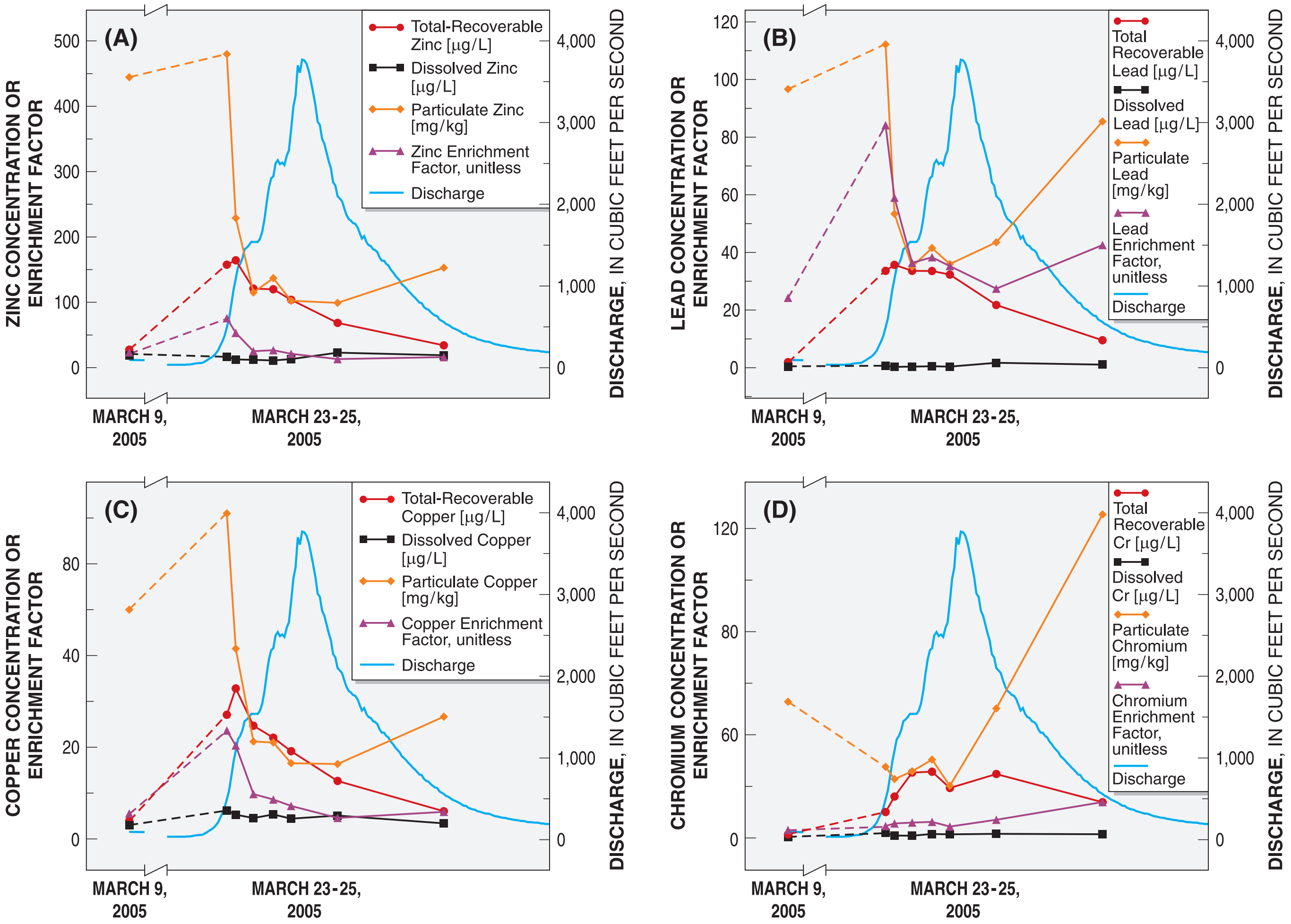

Figure 20. Discharge and phases of (*A*) zinc (Zn), (*B*) lead (Pb), (*C*) copper (Cu), and (*D*) chromium (Cr) during a storm in March 2005 on the Northeast Branch Anacostia River (USGS station 01649500). [Traces are plotted as dissolved concentrations in micrograms per liter (µg/L), total-recoverable concentrations in µg/L, particulate concentrations in milligrams per kilogram (mg/kg), and the ratio of the enrichment factor (unitless); x-axis is broken during the 2-week period between the base-flow sample on March 9 and the storm event of March 23–25, 2005.]

the particulate concentrations of Zn are independent of the quantity of sediment, but are reflective of the shifts in relative abundance of small clay-size particles that strongly sorb the metals. Particles are expected to have higher average concentrations of metals when flows are slower and finer particles dominate. There was a small rise in the concentration of particulate Zn at the very beginning of the storm, as materials were transported in the first flush, but it was diluted quickly by sand-size particles that are more typically metal poor. EFs, being unitless ratios that are normalized to Al, reduce grain-size effects, and compare particulate metal concentrations to background levels. There was an initial rise in the enrichment of Zn at the beginning of the storm, indicating a shift in the sources of the fine particulates, but this recovered quickly to base-flow enrichments very early in the storm. This may indicate an early effect from the first flush of local runoff into the river that shifted to more regional background ratios for this urban stream.

Pb, which also is very particle-reactive, behaved similarly to Zn during the storm, with some exceptions (fig. 20B). EFs for Pb were higher than those calculated for Zn, which is consistent with earlier observations by Velinsky and others (1994). Dissolved phases for both Zn and Pb were not affected by the storm process. Because solubilities for both Zn and Pb are very low, they are most likely saturated in the dissolved phase, and do not change with shifts in flow.

The geochemistry of Cu during the storm (fig. 20C) varied somewhat from that of Zn and Pb. Cu readily chelates, and often has a significant dissolved phase when there are dissolved organic compounds available for complexation. The dissolved phase of Cu increased during the storm, and remained elevated throughout the event until the river returned to base-flow conditions. Particulate concentrations and enrichments of Cu were low until the onset of the storm. Cu rose quickly at the beginning of the storm, as runoff contributed the first flush, and then receded quickly as particle sizes increased, and as sources possibly shifted from the initial runoff. Cu is a common urban contaminant, sometimes enhanced from the passage of water through copper plumbing systems and from brake-pad wear residuals in road runoff.

Cr (fig. 20D) exhibited a somewhat different pattern during the storm, with particulate concentrations declining at the very beginning of the storm. Total-recoverable Cr increased slightly during the storm as overall particle loads increased, but the Cr EFs were almost unaffected by the storm, indicating that runoff from local sources in the Anacostia River watershed was not an important contributor of Cr.

Although analysis of a single storm provides insight, the patterns in concentrations of SS, nutrients, and metals vary between individual storms. Concentrations and behavior vary due to: (1) differences in the intensity of each storm; (2) the antecedent conditions, such as the length of dry period prior to the storm and the intensity of previous storms; and (3) the amount of material in storage in bed sediment.

Shiller (1997) observed seasonal and spatial variations in dissolved metals in the Mississippi River, a large and well-integrated river system. The Mississippi River has three major tributaries that vary in their contribution of flow, and Shiller (1997) observed non-conservative behavior in most of the metals; he attributed this in part to seasonality, shifts in redox, and to temperature (biological activity). Concentrations of solid-phase metals in the Mississippi River were fairly stable, indicating more regional sources. Concentrations of ammonium were in phase with temperature, likely mirroring shifts in seasonal productivity. Water chemistry in larger, more integrated streams with less urban development than the Anacostia River is controlled primarily by variations in redox, temperature, and biological activity. Large rivers also tend to be more homogeneous as it takes more massive quantities of water and(or) sediment to shift the concentrations of chemicals in transport. In contrast, urban streams appear to show shifts in stream chemistry during storm events that are more likely related to local shifts in sources.

Estimation of Continuous Concentrations of Nutrients and Suspended Sediment

The collection of continuous water-quality data at 15-minute intervals can provide a detailed picture of hydrologic processes, but is generally limited to physical parameters that are easily measured with water-quality data sondes. In some cases, it is possible to deploy instruments that can do micro-chemical tests, such as selected colorimetric analyses of nutrients, but these are costly and require a higher degree of maintenance with chemical reagents and frequent calibration. Ion-selective electrodes (ISEs) for some parameters such as ammonia and nitrate also are options. Measurements using ISEs are prone, however, to matrix effects and are sometimes inaccurate. Recently, the USGS has used multiple-regression models to predict water-quality concentrations and loads for nutrients, pesticides, metals, and bacteria from continuous physical parameters such as turbidity and flow (Christensen and others, 2000; Christensen, 2001; Rasmussen and Ziegler, 2003; Rasmussen and others, 2005).

In the current study, linear regression relations on log-transformed variables were determined to estimate SS, TN, and TP from continuous physical parameters at both Anacostia River stations. Final equations with statistics on the estimates are presented in table 5. Continuous variables—discharge, water temperature, pH, SC, and turbidity—were tested against the concentrations of nutrients and SS in a stepwise-regression model. Concentration of dissolved oxygen was not used because of gaps in the dataset. Turbidity was a significant explanatory variable for the concentrations of SS and nutrients. Turbidity is an indicator of the suspended material in the water column. It is determined by shining an incident beam of light into a parcel of water and measuring the reflected light at an angle of 90 degrees to the incident light. It is less sensitive

Table 5. Regression equations and statistics for the estimation of suspended sediment, total phosphorus, and total nitrogen at the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively).

[mg/L, milligrams per liter; SS, concentration of suspended sediment in mg/L; TP, concentration of total phosphorus in mg/L; TN, concentration of total nitrogen in mg/L; Q, discharge in cubic feet per second; Turb, Turbidity in formazin nephelometric units (FNU); %, percent; multiple R^2, coefficient of determination; actual relative bias, relative bias of the residuals]

	Regression equation	Multiple R^2	Actual relative bias	Degrees of freedom
	Northeast Branch Anacostia River (Station 01649500)			
Suspended sediment	$\log_{10}SS = -0.8655 + 0.4228\log_{10}Turb + 0.8201\log_{10}Q$	0.95	-5.5%	70
Total phosphorus	$\log_{10}TP = -2.0342 + 0.2798\log_{10}Turb + 0.2924\log_{10}Q$	0.88	-3.7%	61
Total nitrogen	$\log_{10}TN = 0.0419 + 0.1427\log_{10}Turb$	0.67	-3.8%	68
	Northwest Branch Anacostia River (Station 01651000)			
Suspended sediment	$\log_{10}SS = -0.4754 + 0.6827\log_{10}Turb + 0.5252\log_{10}Q$	0.95	-3.4%	67
Total phosphorus	$\log_{10}TP = -2.1355 + 0.4591\log_{10}Turb + 0.227\log_{10}Q$	0.92	-3.8%	58
Total nitrogen	$\log_{10}TN = 0.0755 + 0.1646\log_{10}Turb$	0.65	-3.8%	64

to sand-size and larger particles because these do no stay suspended within the instrument, and they do not scatter light as effectively as finer particles (Anderson, 2005). Thus, turbidity is an excellent indicator of the fine particles in the water column, which include clays, silts, mineral flocs, finely divided organic matter, and microscopic organisms. Contaminants such as metals and nutrients tend to adhere to the surfaces of these finer materials, and thus, turbidity may correlate well with their concentrations.

For SS, the use of a second variable, discharge, is physically supported, because turbidity does not quantify the transport of sand-size particles. The addition of discharge to the multiple-regression model refined the estimates with some explanation of the variability due to changes in energy in the system at peak flows. As discussed in the previous section on the water and sediment patterns of chemistry during storms, however, there are pronounced hysteretic effects over the course of each hydrograph, and shifts in the distributions of particle sizes.

This line of reasoning would be expected to be less true for TP, which is sequestered to charged surfaces, particularly to iron-sesquioxide flocs, and is thus predominantly transported on the finer particles. As expected, the inclusion of discharge in the TP equations did not significantly increase the coefficient of determination (multiple R^2), but it did decrease the average relative bias of the estimate by about one half, making the inclusion of both turbidity and flow a better model choice.

For both river stations, there was a weak relation between TN and SC when the spurious values for high SC due to road salt were removed. When this adjusted SC was included in the equation, it increased the overall multiple R^2, but not enough to compensate for the exclusion of sample data with high SC values. The relative average bias for both model versions was virtually the same. On the basis of these observations and the principle of parsimony, the adjusted SC was not included in the model for TN at either site.

The values of multiple R^2 should be considered carefully because these were determined in log space. When the concentrations were retransformed back to real space, the variance was increased, particularly at high concentrations.

Comparisons of estimated concentrations to observed values within the context of stream hydrology provide some insight into the accuracy of these models. Time-series overlays of discharge and the predicted and observed concentrations of SS, TN, and TP at both of the Anacostia River stations are shown in figures 21–26. The traces for three storms in spring 2005 for the Northwest Branch Anacostia River are shown in figure 21A, and a closer look at the March storm is shown in figure 21B. Residuals (the difference between observed and estimated values) overall were generally within 10 percent or less of the ambient concentrations. Both the estimated and observed concentrations showed a hysteresis with their relation to discharge over the course of the storm. In this example, the concentration of SS remained elevated well after the flow had peaked, and even beyond the point when conditions returned to base flow. This plot also shows that the use of real-time estimation provided more details about the short-term shifts in the concentration over time. The initial rise in the hydrograph was not completely smooth. Changes in the levels of SS reflected the shifts in flow and energy on the rising limb and possibly shifts in the sources of sediment over time.

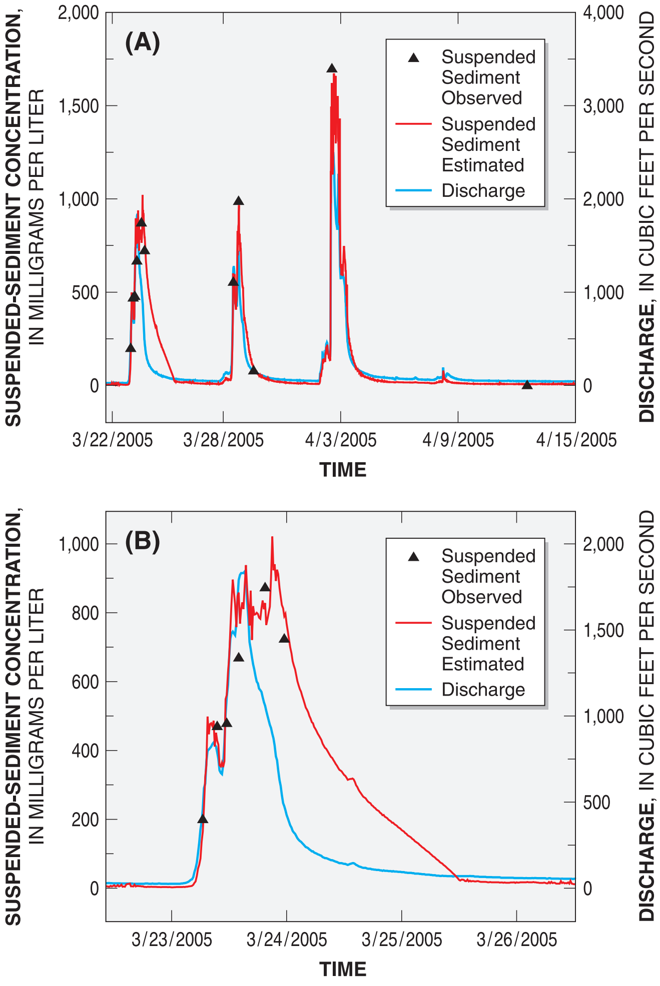

Figure 21. Time-series overlay of discharge with estimated and observed concentrations of suspended sediment on the Northwest Branch Anacostia River (USGS station 01651000). (*A*) Traces of three storms in spring 2005, and (*B*) greater detail of one storm in March 2005.

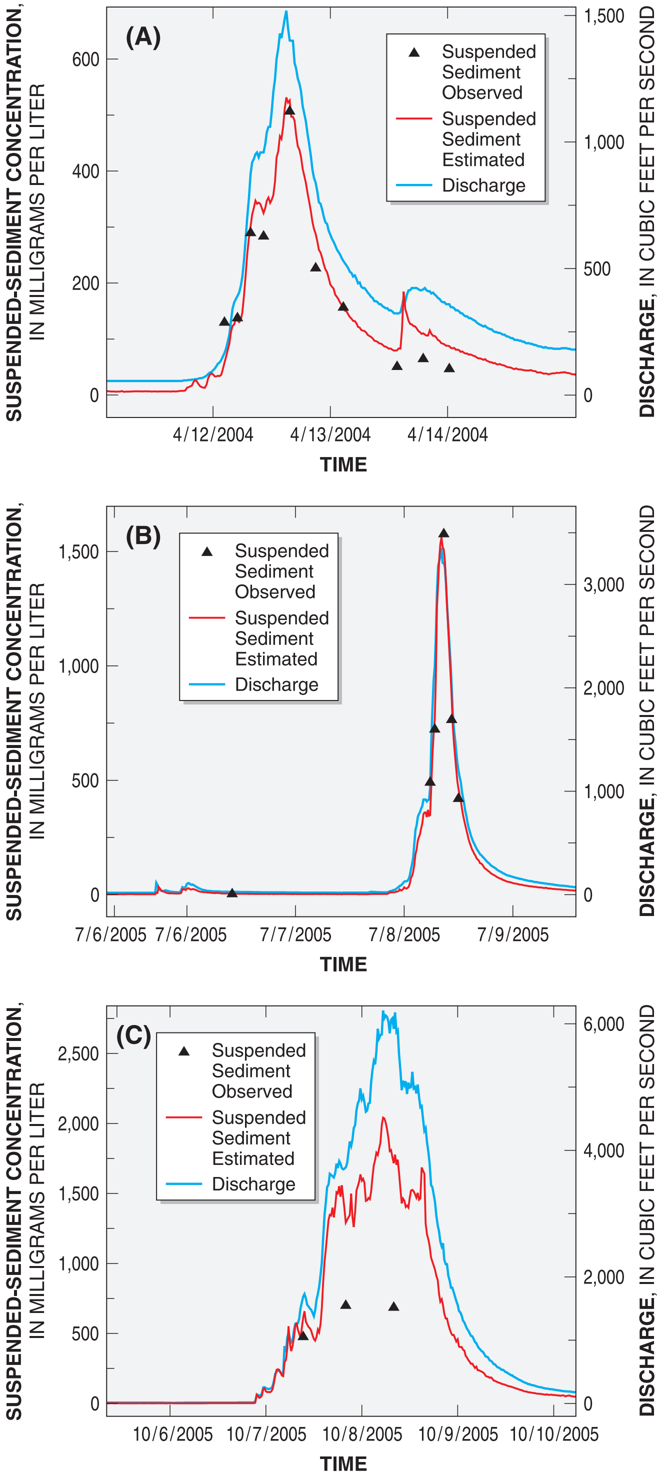

Figure 22. Time-series overlay of discharge with estimated and observed concentrations of suspended sediment on the Northeast Branch Anacostia River (USGS station 01649500). (*A*) Traces of a spring storm in 2004, (*B*) a summer storm in July 2005, and (*C*) a fall storm in October 2005.

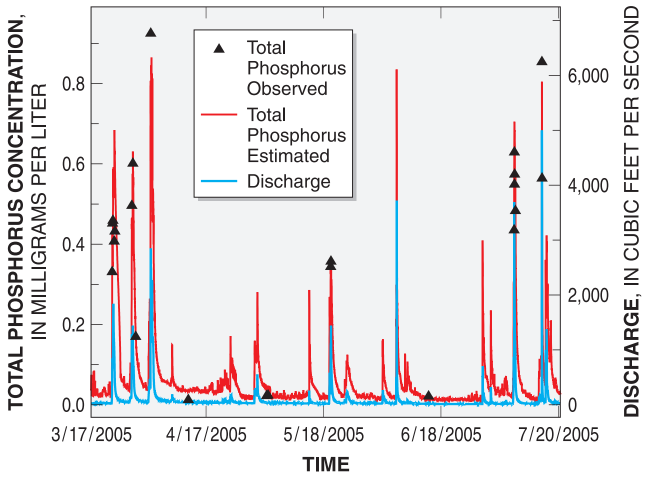

Figure 23. Time-series overlay of discharge with estimated and observed concentrations of total phosphorus on the Northwest Branch Anacostia River (USGS station 01651000). Trace of a series of spring and summer storms in 2005.

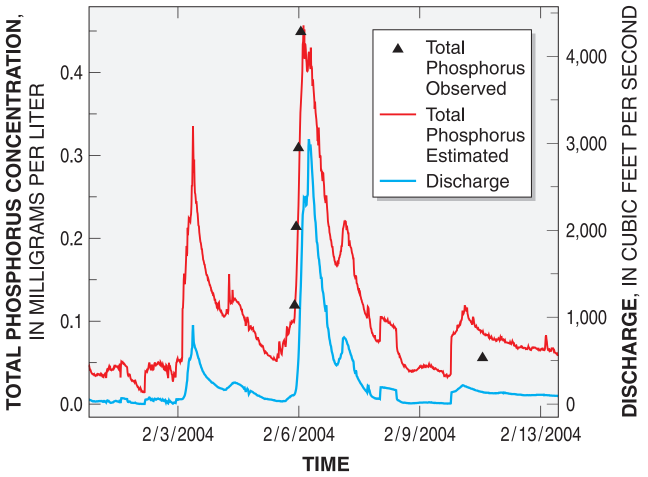

Figure 24. Time-series overlay of discharge with estimated and observed concentrations of total phosphorus on the Northeast Branch Anacostia River (USGS station 01649500). Trace of a series of winter storms in 2004.

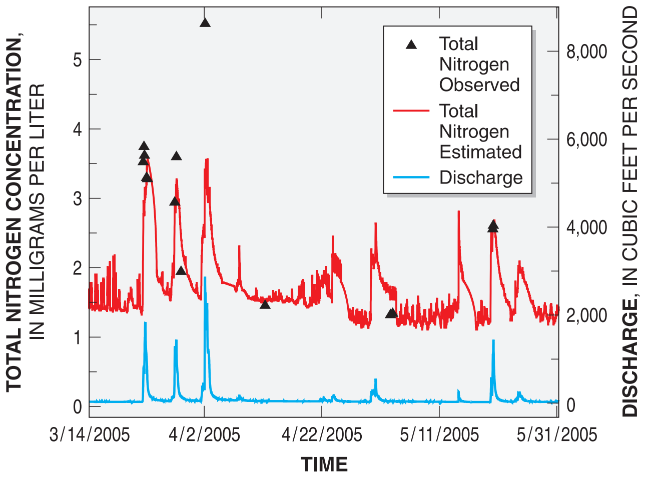

Figure 25. Time-series overlay of discharge with estimated and observed concentrations of total nitrogen on the Northwest Branch Anacostia River (USGS station 01651000). Trace of a series of low-intensity storm events in spring 2005.

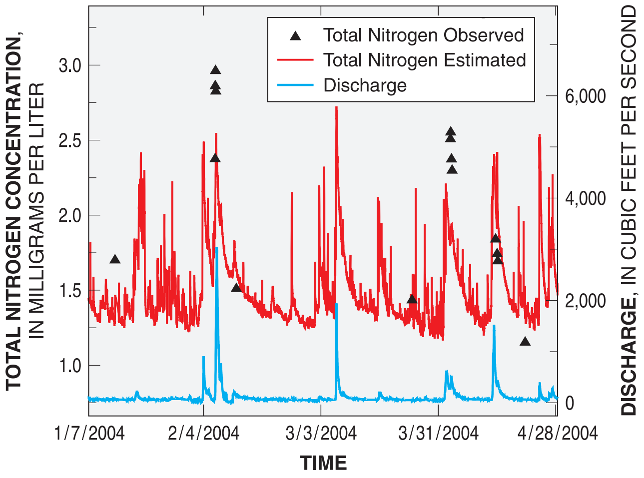

Figure 26. Time-series overlay of discharge with estimated and observed concentrations of total nitrogen on the Northeast Branch Anacostia River (USGS station 01649500). Trace of a series of low-intensity storm events in winter and spring 2004.

Comparisons between estimated and observed concentrations of SS during three different seasons at the Northeast Branch station are shown in figures 22A–C. In the first example (spring 2004, fig. 22A), the model estimations for the first storm are quite good, again capturing the hysteretic behavior of SS with residuals that are generally much less than 10 percent, but in subsequent storms, estimated values vary by as much as 50 percent, particularly during the event on April 14. In the second example (summer 2005, fig. 22B), modeled and observed concentrations tracked very closely, within 10 percent, but in the third example (fall 2005, fig. 22C) the residuals were off by more than 100 percent for two measurements during the peak of the storm. Peaks in turbidity and flow were 470 FNU and 6,210 ft^3/sec, respectively, which indicates very high flows, but lower than normal peak values in turbidity. At these high flows, it is expected that a large fraction of the SS would be sand-size, and it is possible that this error was due to the inefficiency of the autosampler to draw large-grained materials up through the lines, rather than to the multiple-regression model. It was not determined whether seasonal differences in the relation were part of the errors or if the discrepancies were due to random error. Generally over the 2-year period of the current study, the model was a very good estimator of the concentrations of SS, with residuals of much less than 10 percent, but with some exceptions. It is apparent from the different hydrographs that the hysteretic effects were variable between storms, emphasizing again the limitations of discharge rating curves to estimate SS that do not include turbidity (Horowitz, 2003). Rating-curve analyses based on flow and(or) turbidity are best statistical fits to a dataset, so over- and under-predictions are expected for individual value estimates.

Similar time-series plots for TP and TN are shown in figures 23–26. For TP (figs. 23 and 24), the model predictions are still fairly good with some consistent over-estimation at base-flow concentrations and under-estimation for the high outliers. Some events seem to fit the models better than others, and residuals on average are around 10 percent of the observed values. For the February 7, 2004 storm on the Northeast Branch (fig. 24), the concentrations of TP were estimated fairly well on the rising limb of the hydrograph; however, for a storm that followed several days later, the concentrations were over-predicted by about 50 percent more than the observed value on the falling limb.

The plots for the prediction of TN (figs. 25–26) show that the model for TN was not as good as for SS and TP, as evidenced by the lower R^2 values (table 5). The models for predicted TN appear to be less accurate on the falling limbs of the hydrographs, and occasionally for extreme values where estimated values were under-predicted by as much as 60 percent, obviously missing some important predictor of the variance in TN. The biases for the predictions of TN were similar to SS and TP, so errors may be expected to average out somewhat over time, such as when these data would be used to calculate annual loads and yields.

The sampling regime in the current study was weighted towards base-flow sample collection in the morning to early afternoon hours, which is a weakness in the dataset. Short-term variability observed in pH, temperature, turbidity, and the concentration of dissolved oxygen indicates that there are important shifts in the stream chemistry over the diurnal cycle during base flow. Water-quality samples collected more frequently over the entire diurnal cycle would improve the understanding of hydrologic and biologic processes in the Anacostia River.

Estimation of Contaminant Loads and Yields

Estimates of annual loads (converted to yields) of SS, TN, and TP were calculated for the Northeast and Northwest Branches of the Anacostia River using two versions of the USGS AMLE unbiased log-linear load models, ESTIMATOR and LOADEST. ESTIMATOR uses mean daily flow and time as predictors of concentration, and in the current application, LOADEST used hourly steps of discharge and turbidity as predictors. Flow was left out of the LOADEST calculations for TN, because the regression analysis did not find this to be a significant predictor. LOADEST estimates for 2004 at the Northwest Branch were not possible because measurement of continuous turbidity was not started until February of that year.

Results for each parameter were mostly similar between the two methods (table 6), as would be expected from the similar forms of the models, but there were some notable exceptions. Yields determined by LOADEST were consistently higher for each parameter and at each station than by ESTIMATOR. However, differences were not large and values were within the 95-percent confidence intervals of each other. The most notable difference between the two estimates was that the SEP, expressed as confidence intervals for LOADEST, were much smaller than those from ESTIMATOR (table 6). Given the greater detail of information with hourly time steps in the predictors, and observations that turbidity explains more of the variance in concentrations, LOADEST would be expected to produce more accurate and precise yield estimates than ESTIMATOR. Rasmussen and others (2005) compared different modeling approaches to predict loads and found that: (1) load estimates based on discrete samples that do not target storm events under-estimate the true loads, (2) loads based solely on discharge over-estimate loads, and (3) loads based on continuous turbidity are in between the other two estimates and have much smaller errors associated with them. These differences between the models for the load estimates were not observed in the current study, but the confidence intervals were smaller with the LOADEST models.

For perspective, annual yields for the stations on the Northeast and Northwest Branches of the Anacostia River are compared with estimates from other studies for these and

Table 6. Estimates of annual yields (load per square area in kilograms per year per square kilometer) for suspended sediment, total nitrogen, and total phosphorus at the Northeast and Northwest Branches of the Anacostia River (USGS stations 01649500 and 01651000, respectively) for data collected in 2004 and 2005.

[Loads were estimated using two modeling approaches—ESTIMATOR, using mean daily flow and time as predictors of concentration, and LOADEST, using hourly time steps of flow and turbidity as predictors. For comparison to other rivers, yields estimated by the Metropolitan Washington Council of Governments (1998) at the same two river stations, and yields estimated for the Chesapeake Bay River Input Monitoring Program (U.S. Geological Survey, 2006) for the Susquehanna River (USGS station 01578310), Potomac River (USGS station 01646580), Patuxent River (USGS station 01594440), and James River (USGS station 02035000) also are presented. Values in parentheses are the 95-percent confidence intervals based upon the standard errors of the predictions. All loads are calculated for the calendar years (January through December); kg/year/km^2, kilograms per year per square kilometer; km^2, square kilometers; ft^3/s, cubic feet per second; MWCOG, Metropolitan Washington Council of Governments]

	Watershed area, km^2	Mean annual flow, ft^3/s	Suspended sediment, kg/year/km^2	Total nitrogen, kg/year/km^2	Total phosphorus, kg/year/km^2
			2004		
Northeast Branch (ESTIMATOR)	189	104.4	131,000 (51,300–277,000)	959 (873–1,050)	97 (71–130)
Northeast Branch (LOADEST)	189	104.4	224,000 (157,000–310,000)	962 (891–1,040)	110 (89–134)
Northwest Branch (ESTIMATOR)	128	61.3	215,000 (65,700–531,000)	1,080 (936–1,240)	126 (70–209)
Northwest Branch (LOADEST)	128	61.3	—	—	—
Susquehanna	70,189	65,540	37,300	1,390	68
Potomac	29,940	15,470	42,800	952	60
Patuxent	901	431.6	24,000	801	56
James	16,193	8,093	29,800	333	47
			2005		
Northeast Branch (ESTIMATOR)	189	104.7	176,000 (76,800–347,000)	976 (867–1,090)	109 (78–148)
Northeast Branch (LOADEST)	189	104.7	219,000 (156,000–300,000)	1,010 (925–1,090)	117 (94–144)
Northwest Branch (ESTIMATOR)	128	71.3	223,000 (60,500–587,000)	1,200 (1,000–1,430)	161 (80–1,430)
Northwest Branch (LOADEST)	128	71.3	248,000 (164,000–361,000)	1,360 (1,210–1,530)	161 (126–203)
Susquehanna	70,189	45,810	21,100	1,050	40
Potomac	29,940	10,580	23,400	608	24
Patuxent	901	437.7	27,000	787	53
James	16,193	6,239	16,500	227	27
			1998		
Northeast Branch (MWCOG)	189	100.9	81,793	1,636	236
Northwest Branch (MWCOG)	128	58.3	106,356	1,702	248

other Chesapeake Bay tributaries (table 6). Yields at these Anacostia River stations were estimated in the early 1990s by the Metropolitan Washington Council of Governments (1998), and yields for the Susquehanna River at Conowingo, Maryland (USGS station 01578310), the Potomac River at Washington, D.C. (USGS station 01646580), the Patuxent River at Bowie, Maryland (USGS station 01594440), and the James River at Cartersville, Virginia (USGS station 02035000) were estimated for 2004 and 2005 by the U.S. Geological Survey (2006). The Patuxent River station compares well to the Anacostia River stations because it is similarly a small watershed in the Baltimore-Washington, D.C. corridor that is quickly becoming urbanized. The other three stations have much larger watersheds and have more mixed land use, but are still useful for comparison.

Senus and others (2004) compared yields and trends for all of the Chesapeake Bay RIM stations from 1997–2001; the yields of TN, TP, and SS were similar across all of the larger integrated river basins. For 2004, yields for TN on the Susquehanna River were higher than those at any of the other stations, but this can be attributed to a higher than average rainfall and corresponding higher streamflow in this watershed. When the yields were calculated as flow-weighted, they were more similar at all of the RIM stations. According to Langland and others (2006), freshwater flow entering the Bay from the Susquehanna River watershed was particularly high in 2004, with flow during the summer season the highest during a 3-month period recorded since 1937. TN yields in the Susquehanna River were the highest since 1990, and TP and SS yields were the fifth highest. Annual flow-weighted concentrations actually showed significant downward trends for many of the sites for all three parameters.

Yields of TN and TP for the Anacostia River were generally higher than those estimated for the other Fall Line tributaries (table 6), but the differences were not large. Variations in hydrologic conditions between the stations may account for some of the observed differences in yields, but the effects of urban land use also are important.

Yields of SS were higher by an order of magnitude at both of the Anacostia River stations than those at any of the RIM tributaries. The Anacostia River watersheds are within the Atlantic Coastal Plain and Piedmont Plateau Physiographic Provinces as opposed to all of the RIM watersheds, which are above the Fall Line, so comparisons should be made carefully. However, urbanization is an important factor for elevated yields of SS. Increases in impervious surface in the watershed and restructuring of stream channels can destabilize stream banks and increase export of sediment from a watershed.

Gellis and others (2005) used historical data to estimate similar average annual yields for SS from 1963–1975 at the Northwest Branch Anacostia River near Colesville, Maryland (USGS station 01650500) - 246,000 kilograms per year per square kilometer (kg/yr/km^2). The Colesville station is a short distance upstream from the station monitored in the current study near Hyattsville. Some of the high yields of SS during the current study could be attributed to stream-restoration projects in the Northwest Branch, but as high yields were found at both stations and are consistent with earlier estimates at another station in the Northwest Branch, other factors also must be considered.

Information Learned for the Anacostia River and Urban Streams

This report has summarized data collected from July 2003 through December 2005 at two stations on the Anacostia River. The stations are above the head of tide on the Northeast and Northwest Branches of the Anacostia River, and data collected at these sites encompass the majority of the nontidal, upper watersheds of the Anacostia River. The sampling strategy used in this study is novel for this watershed, in that real-time measurements of physical parameters with water-quality monitors were collected concurrently with discrete water-quality sampling for SS, nutrients, and metals, and combinations of these measurements were used to infer information about hydrologic and chemical processes in the streams. Significant statistical relations were found between the continuous data and discrete water chemistry.

The information gained by monitoring over short time scales has allowed more detailed interpretation of the processes in these streams. Observations of large diurnal shifts in parameters such as pH, concentration of dissolved oxygen, temperature, and sometimes turbidity during base flow have provided information on biological productivity in the river ecosystem, as well as a glimpse into periodic perturbations in the urban environment. There are numerous sources of variation in stream chemistry, particularly in an urban environment, and additional study is needed to break down loads of chemical contaminants into their component sources (fig. 27). Some immediate benefits of real-time data collection included: (1) rapid identification of broken sewer lines based on measurements of turbidity and SC, (2) observations of daily rises in chemical parameters such as turbidity that record unidentified activities in the urban watershed, (3) observations of productivity based on dissolved oxygen and pH dynamics that may be enhanced by other urban processes, and (4) more accurate yield estimates of SS and nutrients. Future applications of these data could include more quantitative estimates of productivity from diurnal variations in the concentration of dissolved oxygen, which may have important applications for the management of nutrient-induced eutrophication in the Anacostia River.

Another important result from continuous-data collection (turbidity and streamflow) has been more accurate estimates of loads and yields. Comparisons of estimates with the model ESTIMATOR, which uses traditional rating curves based on mean daily flow to estimates with the model LOADEST, that are based on hourly interval measurements of flow and turbidity, have shown significantly improved loading estimates with the smaller time steps. The results provided annual estimates

Figure 27. Exposed sewer manhole stacks in Sligo Creek, a small tributary on the Northwest Branch Anacostia River. (Photograph courtesy of the Anacostia Watershed Society.)

of yields of SS, TP, and TN at both stations, and concentrations of these three parameters have been estimated in real time on a USGS website, providing current and continuous information on water quality in the Anacostia River.

The current study demonstrated the need to collect more data over shorter diurnal time cycles to capture new, shorter-term sources of variance, and the need to collect a higher density of samples for parameters that have a high overall variance in concentration. For example, continuous monitoring recorded large diurnal changes in some of the basic field parameters such as temperature, concentration of dissolved oxygen, and pH. These parameters can have substantial effects on the concentrations, partitioning, and bioavailability of metals and nutrients.

The importance of targeting sampling designs on storm events and collecting sufficient data also is evident from the results of this and other studies (fig. 28). Horowitz (2003) presented a summary of the USGS NASQAN work and evaluated the use of rating curves based on flow (turbidity was measured in that study but was not used in the interpretation). Stations with daily sediment collection were used to compare different sampling strategies. Sediment rating curves were found to over-predict low concentrations of SS and to under-predict the high values. Thus, Horowitz (2003) showed that short timeframes for load estimates are undesirable because the biases do not have a chance to balance out. He concluded that the best approach for load estimation would be to use a monthly sampling strategy that was hydrologically based, that sampling plans must include a sufficient number of storm events, and that individual annual rating curves were better than long-term curves because of natural shifts in the ratings over time. There are inherent errors from hysteretic effects in the concentration of SS during storm events, when using only discharge as a predictor. All of these findings are in agreement with the results of the current study.

The Anacostia River is not used for drinking water, but it is an important tributary to the Chesapeake Bay, and an important environment for wildlife in an urban watershed. Yields of sediment and nutrients for the nontidal Anacostia River were estimated for 2004–05 and compared to yields from other local or regional studies. Yields of nitrogen and phosphorus were slightly higher but similar to those found in other watersheds of the Chesapeake Bay, but the yields of SS were higher by an order of magnitude in the Anacostia River. Urbanization has been a factor in the mobilization of sediments in the Anacostia watershed, as evidenced by ongoing development disturbance of the land surface and changes in stream channels that increase the energy during storms (figs. 2 and 6; Gellis, 2005).

Other studies have observed high sedimentation rates in the lower tidal portions of the Anacostia River where velocities are slower and high sediment loads from the nontidal watershed accumulate (Velinsky and others, 1999). Comparisons of yield estimates between the two Anacostia River stations in the current study showed very similar results to those of Velinsky and others (1999). As observed in this and other studies, contaminants such as nutrients and trace metals are usually associated with the particulate phases and an understanding of the fluxes and deposition patterns of SS would be important to evaluate transport processes.

The upper Anacostia River watershed is similar to urban watersheds across the United States (Mahler and others, 2006). The geochemistry of nutrients and trace metals in streams is very complex, with processes that transfer chemical constituents between phases in the water column and bed sediments, as well as in and out of the river system. These processes have been described as “material spiraling” (Hart and Hines, 1995), whereby there is a dynamic interaction between the biogeochemical cycling of chemicals and downstream advection. In this model, contaminants within the stream will typically be distributed within 3 compartments: the water compartment, wherein metals and nutrients are present as dissolved or colloidal phases; the seston compartment of suspended biological or abiotic particulate materials; and the benthic compartment, wherein metals and(or) nutrients may be temporarily or permanently stored or at least retarded in transport. Within each

Figure 28. Storm event at Northeast Branch Anacostia River in winter 2003. High turbidity and suspended-sediment concentrations occur during stormflow. Suspended sediment is a carrier for many particle-reactive contaminants such as trace metals and nutrients. (Photograph courtesy of Al Dombroski, Jr., Riverdale, Maryland.)

stream segment, many biogeochemical processes can modulate the transfer of contaminants between the compartments, including chemical transformations, adsorption and desorption, and biological uptake and release. Superimposed on all of these processes is the net downstream flux of water, sediment, and associated contaminants, as well as fluxes to and from the river from external sources. The complex shifts in particle size and composition observed during storms in the Anacostia River demonstrate these dynamic interactions between physical and chemical processes. The time scales for variations in constituent concentrations span short diurnal cycles to longer annual and interannual time frames with climatic changes. Understanding the dynamics of these processes requires the measurement of water quality on the same time scales and in dissolved as well as particulate phases. Data programs must be designed to best capture the sources of variability. Understanding of the interactive processes that modulate the concentrations and loads or yields of contaminants and the spatial and temporal scales of variability is important to water-resources managers in developing strategies to improve river ecosystems.

Summary

In 2003–05, the U.S. Geological Survey partnered with the Prince George’s County Department of Environmental Resources, the Maryland Department of the Environment, the U.S. Environmental Protection Agency, and George Mason University to monitor water quality in the Anacostia River. Two stations, both with long historical records of discharge, were upgraded with automated sampling equipment to collect data for suspended sediment, nutrients, trace metals, and continuous physical parameters. These stations are the Northeast Branch Anacostia River at Riverdale, Maryland (U.S. Geological Survey station 01649500) and the Northwest Branch Anacostia River near Hyattsville, Maryland (U.S. Geological Survey station 01651000). Some of the data collected at these stations have been used to quantify the contributions of sediment and nutrients from the upper watershed of the Anacostia River in Maryland to the more heavily urbanized tidal area within Washington, D.C., and to interpret transport processes and sources of contamination for suspended sediment, nutrients, and trace metals.

Data were evaluated to determine the primary phases of nutrients and metals in transport, the behavior of suspended sediment and chemicals over time and varying flow regimes, and enrichment factors for trace metals. Particulate Kjeldahl nitrogen was found to be an important transport phase for nitrogen in both streams during storm events. This pattern is likely typical of urban streams as compared to streams that are more dominated by agriculture or undeveloped land. During storm events, particulate phases were important carriers for nutrients and metals. Detailed analysis of a single storm showed that concentrations of nutrients and metals were highest during the leading edge of the storm, decreased early as more sand-size material was incorporated in the sediment load, and further decreased during storm recession as the concentration of total suspended sediment decreased.

Unbiased multiple-regression models were developed to estimate annual yields of suspended sediment, total nitrogen, and total phosphorus at each station in 2004 and 2005. These yields were compared to similar calculations for other tributaries within the Chesapeake Bay watershed, including the Susquehanna, Potomac, Patuxent, and James Rivers. Yields for total nitrogen and total phosphorus in the upper Anacostia River watershed were generally higher than in most of the other tributaries, except for the Susquehanna River, which experienced a higher than normal flow during that time period. Suspended-sediment yields were higher at both branches of the Anacostia River, by approximately a factor of 10, than at any of the other Chesapeake Bay tributaries. Some of the differences in yields may be due to differences in surficial geology between the watersheds, but urban development is an important influence on the Anacostia River.

Linear regression relations on log-transformed variables were determined to estimate concentrations of suspended sediment, total nitrogen, and total phosphorus from continuous field parameters at both Anacostia River stations. Turbidity was the most significant explanatory variable for all three parameters, highlighting the importance of fine particulate matter as a carrier for contaminants in river systems. In some cases, the use of discharge as a second variable was significant and physically supported, because turbidity does not measure sand-size particles. Discharge is a good indicator of changes in energy in a river system, particularly at peak flows. There were, however, pronounced hysteretic effects over the course of each hydrograph and estimates of concentration were better during some storms than others. Factors that affected the statistical relations include antecedent conditions such as the size and timing of previous storms, seasonality, and shifts in sediment sources over the course of each storm. Estimated concentrations of suspended sediment, total nitrogen, and total phosphorus in near-real time for the Northeast and Northwest Branches of the Anacostia River may be viewed on the world wide web at *http://md.water.usgs.gov/rtqwmodeling/*.

The current study has provided information on contributions of potential contaminants from the upper watershed of the Anacostia River. Data from the upper watershed were compared to conditions in the lower tidal Region of Concern in the Anacostia River as well as to other tributaries in the Chesapeake Bay watershed, and to urban streams across the United States. The upper Anacostia River may be characterized as a light-urban stream with moderate concentrations of nutrients and trace metals in transport. Estimation of the quantities and comparative magnitudes of contaminants within the context of transport processes of the river system will aid water-resources managers in focusing strategies where improvements may be most beneficial and cost-effective.

Acknowledgments

The authors wish to thank the following people for their assistance and contributions to this investigation and report. Dr. Mow-Soung Cheng of the Prince George's County Department of Environmental Resources and Narendra Panday and George Harman of the Maryland Department of the Environment have provided support and encouragement for developing new study approaches on this project. USGS hydrologic technicians David Brower, George Zynjuk, Jon Evans, and Deborah Bringman provided support in helping to design the field efforts and in collecting data. Jonathan Dillow and James Jeffries provided review and quality assurance of the data. Maps were created by Andrew LaMotte and Timothy Auer of the USGS. The authors thank Arthur Horowitz, Andrew Ziegler, Bradley Garner, James Gerhart, Robert Shedlock, Valerie Gaine, Jonathan Dillow, and Dorothy Tepper, all of USGS, for thoughtful reviews that enhanced the quality of this report.

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Appendix. Water-quality criteria and guidelines for dissolved trace metals in freshwater.

[Recommended guidelines and criteria for the protection of aquatic life in freshwater. Toxicity for most of these metals varies as a function of hardness in the water column. Canadian Council of Ministers of the Environment values for copper, lead, and nickel are presented as ranges that vary as a function of alkalinity. These values are based on a value of 100 milligrams per liter of hardness; ammonia is not included in this table because the toxicity of ammonia is strongly pH-dependent; all units are in micrograms per liter; CMC, Criteria Maximum Concentration (acute); CCC, criterion continuous concentration (chronic); —, not available]

	USEPA[a]		CCME[b]
	CMC	CCC	Guidelines
Aluminum	750	87	—
Arsenic	340	150	5.0
Cadmium	2.0	0.25	0.017
Chromium (III)	570	74	8.9
Chromium (VI)	16	11	1.0
Copper	13	9.0	2–4
Lead	65	2.5	1–7
Nickel	470	52	25–150
Zinc	120	120	30

[a] U.S. Environmental Protection Agency (USEPA, 2006)

[b] Canadian Council of Ministers of the Environment (CCME, 2006).

Prepared by Publishing Service Centers 3 and 1.
Edited by Valerie M. Gaine.
Graphics by Timothy W. Auer.
Layout by Ann Marie Squillacci.

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Miller, C.V., Gutiérrez-Magness, A.L., Feit Majedi, B.L., and Foster, G.D.—**Water Quality in the Upper Anacostia River, Maryland: Continuous and Discrete Monitoring with Simulations to Estimate Concentrations and Yields, 2003–05**—USGS Scientific Investigations Report 2007–5142