USGS
science for a changing world

Prepared in cooperation with the
National Park Service

Estimates of the Loads of Nitrite + Nitrate in the Flow of Bassett Creek to the Maryland Coastal Bays Adjacent to Assateague Island National Seashore, Water Years 2003–2004

Scientific Investigations Report 2006–5080

U.S. Department of the Interior
U.S. Geological Survey

Estimates of the Loads of Nitrite + Nitrate in the Flow of Bassett Creek to the Maryland Coastal Bays Adjacent to Assateague Island National Seashore, Water Years 2003–2004

By Jonathan J.A. Dillow and Jeff P. Raffensperger

Prepared in cooperation with the

National Park Service

Scientific Investigations Report 2006–5080

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
P. Patrick Leahy, Acting Director

U.S. Geological Survey, Reston, Virginia: 2006

For product and ordering information:
World Wide Web: http://www.usgs.gov/pubprod
Telephone: 1-888-ASK-USGS

For more information on the USGS--the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:
World Wide Web: http://www.usgs.gov
Telephone: 1-888-ASK-USGS

Suggested citation:
Dillow, J.J.A., and Raffensperger, J.P., 2006, Estimates of the loads of nitrite + nitrate in the flow of Bassett Creek to the Maryland Coastal Bays adjacent to Assateague Island National Seashore, Water Years 2003–2004: U.S. Geological Survey Scientific Investigations Report 2006–5080, 10 p.

Contents

Figures

Tables

Conversion Factors and Datums

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
	Mass	
pound (lb)	0.4536	kilogram (kg)
pound (lb)	453,600	milligram (mg)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
acre	0.004047	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
cubic foot (ft^3)	28.317	liter (L)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

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

$$°C=(°F-32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation, as used in this report, refers to distance above the vertical datum.

Water year, as used in this report, is the 12-month period October 1 through September 30, and is designated by the calendar year in which it ends.

Estimates of the Loads of Nitrite + Nitrate in the Flow of Bassett Creek to the Maryland Coastal Bays Adjacent to Assateague Island National Seashore, Water Years 2003–2004

By Jonathan J.A. Dillow and Jeff P. Raffensperger

Abstract

Bassett Creek near Ironshire, Maryland, drains a 1.22-square-mile watershed that enters Newport Bay at the northern end of the larger Chincoteague Bay. Twenty-nine water samples collected from Bassett Creek through a range of low and high flows were analyzed for their content of dissolved forms of nitrogen. The concentrations of nitrite + nitrate in the samples ranged from 0.397 to 3.02 milligrams per liter as nitrogen, and frequently exceeded published thresholds for determining the effects of human activities on watersheds in the area.

Concentrations of nitrite + nitrate in the stream under base-flow conditions varied inversely with flow magnitude, with a statistical correlation between base flow and nitrite + nitrate concentration with $R^2 = 0.90$. Concentrations of nitrite + nitrate in the stream under stormflow conditions had a statistical correlation with water temperature with $R^2 = 0.25$. Both correlations are statistically significant at or above the 95-percent confidence interval. The latter correlation may reflect the seasonal availability of nitrite + nitrate as determined by agricultural practices in the watershed.

The estimated nitrite + nitrate loading rates for water years 2003 and 2004 were 9.3 kilograms per day (total load of 3,400 kilograms per year or 7,500 pounds per year) and 13.9 kilograms per day (total load of 5,100 kilograms per year or 11,200 pounds per year), respectively. The base-flow component of the estimated load of nitrite + nitrate comprised approximately 61 percent and 24 percent of the total estimated nitrite + nitrate load in water years 2003 and 2004, respectively. A seasonal pattern of estimated monthly nitrite + nitrate loading was observed over the study period, with both inferred stormflow and total estimated loads of nitrite + nitrate increasing over the winter and early spring months. Most of the estimated nitrite + nitrate load during the late summer, fall, and early winter is transported in base flow, although fall storms may result in significant stormflow loads, such as occurred in September 2003 and the late summer and fall of 2004.

The flow-weighted concentrations of nitrite + nitrate for Bassett Creek during the study period (1.35 milligrams per liter as nitrogen in water year 2003 and 1.74 milligrams per liter as nitrogen in water year 2004) are similar to the maximum value for the period spanning calendar years 1985 through 2004 for the Choptank River near Greensboro, MD (1.30 milligrams per liter as nitrogen), and lower than the range of values for calendar years 1997 through 2001 for Chesterville Branch near Crumpton, MD (4.21 milligrams per liter as nitrogen to 6.71 milligrams per liter as nitrogen). These comparative values may reflect the effect of the areal extent of agricultural land use in the respective watersheds.

Introduction

Congress established Assateague Island National Seashore (ASIS) on September 21, 1965, to preserve and protect the natural resources and recreational value of Assateague Island. ASIS, which is visited by more than 2 million people annually, showcases one of the few remaining undeveloped barrier-island environments along the Mid-Atlantic Coast.

Chincoteague, Sinepuxent, and Newport Bays lie landward of the Assateague barrier island, and are part of the extensive network of coastal bays that form an important estuary along the Atlantic coast of the Delmarva Peninsula (fig. 1). Collectively these three bays have a total surface area of approximately 36,000 acres, and a watershed of approximately 150 mi^2 (square miles). The bays are shallow, have an average depth of less than 6 ft (feet), and are poorly flushed because of limited freshwater inflow, restricted tidal exchange through two inlets, and an average tidal range of less than 1 ft (National Oceanic and Atmospheric Administration, 1990; Maryland Department of the Environment, 1993). The estuarine resources of Chincoteague and Sinepuxent Bays are integral components of ASIS. More than 35 percent of the Seashore's 48,000 acres consist of the estuarine waters of these two bays.

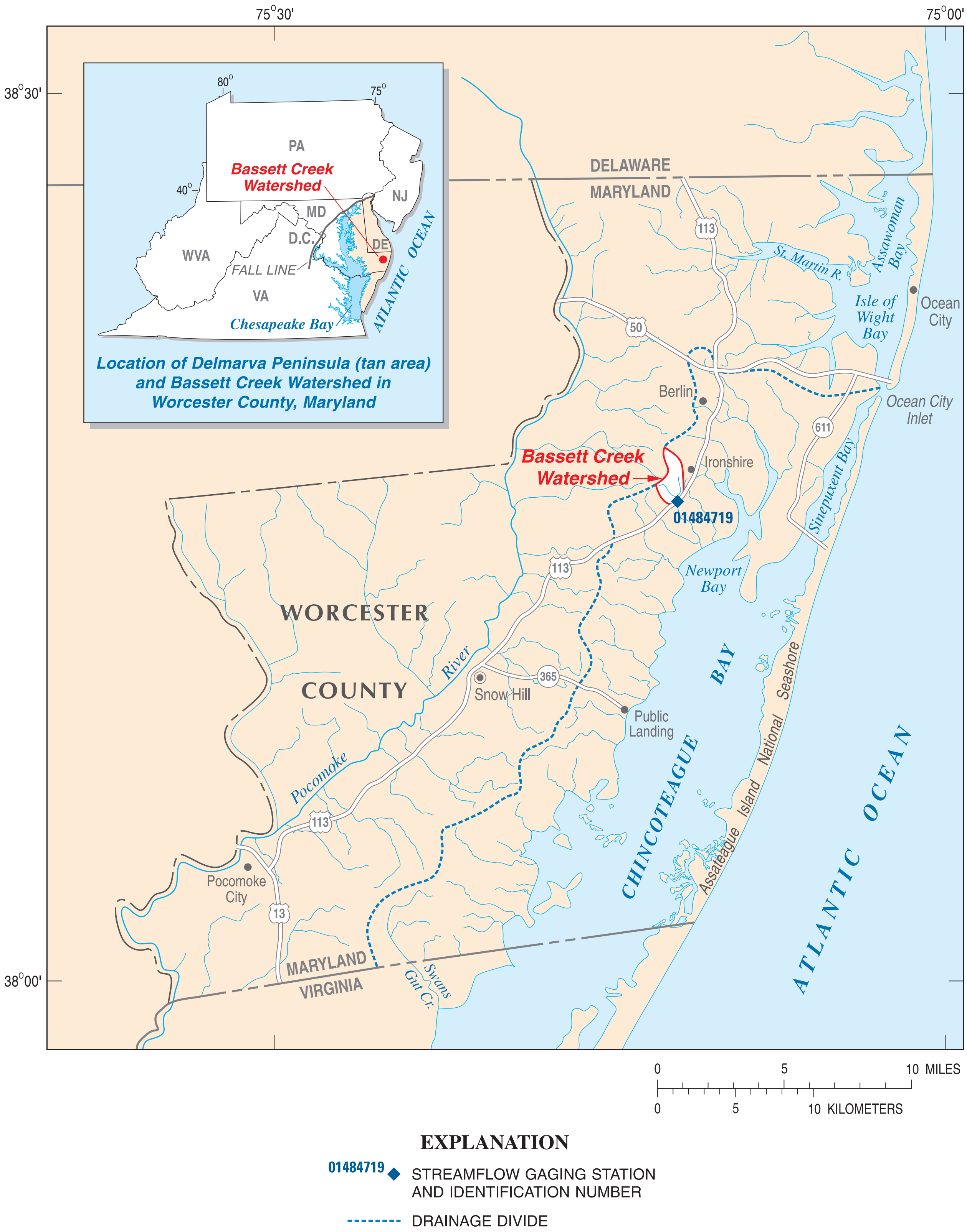

Figure 1. Location of Bassett Creek watershed in Worcester County, Maryland.

Background

Enrichment of nutrients in the shallow restricted estuaries along the Atlantic Coast is a regional problem. Phosphorus and nitrogen are essential for healthy plant and animal growth, but elevated (significantly greater than natural) concentrations of these nutrients can trigger excessive growth of aquatic plants, such as algae, in coastal bays and estuaries, and adversely affect these coastal ecosystems. Abnormally high concentrations of nutrients have been linked to low dissolved oxygen (hypoxic) conditions, which can harm fish and shellfish. High nutrient concentrations also are believed to be one cause for the growth of the dinoflagellate *Pfiesteria*, which is found in Atlantic coastal waters. This form of algae is potentially toxic to fish and other organisms, including humans (Blazer and others, 1998).

The transport pathways of phosphorus and nitrogen differ because of their chemical characteristics. Phosphorus tends to bind to sediment. As a result, phosphorus is transported primarily on fine-grained suspended sediment in storm runoff. In contrast, under oxidizing conditions nitrogen readily forms nitrate[1], which is very soluble and is easily transported down to the water table in sandy soils. Once in ground water, nitrate is transported along flow paths in oxygenated waters and is eventually discharged as base flow into streams, or directly to the coastal bays. Dissolved nitrogen species can also be transported by storm runoff.

Previous and current U.S. Geological Survey (USGS) investigations on the Delmarva Peninsula have shown that ground-water discharge is the major source of nitrate in streams during base-flow conditions (Shedlock and others, 1999; Bachman and Phillips, 1996). These studies indicate that the residence times of ground water in the surficial aquifer range from several years to several decades, so that the effects of nutrient management practices may not be fully reflected in stream base-flow water quality for years or decades following the implementation of those practices, depending on the length of the local ground-water flow paths. In recent USGS studies in the coastal bays drainage area, locally high concentrations of nitrate have been detected in both ground water and stream base flow. Concentration of nitrate in more than one-third of the 22 streams sampled under base-flow conditions during the winters of 1999 and 2000 ranged from 3 to 9 mg/L as N (Dillow and others, 2002). In comparison, in a survey of 296 wells screened in the surficial aquifer on the Delmarva Peninsula, Hamilton and others (1993) determined a threshold value of 0.4 mg/L as N to be indicative of anthropogenic influence.

In recent years, the National Park Service (NPS) and the USGS have been partnering on a series of studies to understand the potential for streams and ground water in the tributary watersheds to contribute excess nutrients to the Maryland Coastal Bays. Previous studies by Dillow and Greene (1999) and Dillow and others (2002) compiled and analyzed existing water-quality data and collected water-quality data from selected sites. The data for nontidal streams indicate that nitrate concentrations are related to land use in the watershed, with nitrate concentrations being generally highest in watersheds with the highest percentages of agricultural land.

From October 2002 through September 2004, the USGS, in cooperation with the NPS—Assateague Island National Seashore, conducted a study of the flow and quality of water in Bassett Creek, which drains to Newport Bay (fig. 1). The study site near Ironshire, Maryland (USGS streamgaging station number 01484719), is the drainage outlet for a 1.22-mi^2, nontidal watershed. The purpose of the study was to estimate loads of nitrite + nitrate in the stream during the study period.

Purpose and Scope

The report describes the streamflow and water-quality data-collection and analysis activities at Bassett Creek near Ironshire, MD, from October 2002 through September 2004. The report also presents the analytical results of the study, including the estimated monthly loads of nitrite + nitrate under base-flow and stormflow conditions, which were calculated by using a statistical regression model (Cohn and others, 1992, 1989).

Description of Study Area

The study area is a watershed located approximately 4 mi (miles) south of Berlin, MD, on the west side of U.S. Highway 113 on the southeastern Delmarva Peninsula. The watershed drainage area is 1.22 mi^2, with a maximum elevation of 42 ft and an outlet elevation of 3.33 ft. The data-collection site is not affected by tidal fluctuations. Land use in the watershed is predominantly agricultural and forested. Row crops cover more than 48 percent of the watershed, while 41 percent of the watershed is characterized as forested. The remainder of the watershed consists of pasture, wetlands, and residential areas. Soils in the watershed consist of moderately permeable sands and sandy silt-clays on gently sloping areas, and relatively non-permeable clay-silts on the nearly level uplands near the watershed divide.

Streamflow and Water-Quality Measurements

Streamflow and water quality were measured at Bassett Creek near Ironshire, MD, during water years 2003 and 2004. The site was instrumented in September 2002 with a suite of sensors that continuously measured and recorded stream stage, water temperature, specific conductance,

[1] In this study, water samples were analyzed for both nitrite and nitrite + nitrate. Concentrations of nitrite only were typically very small, often less than the laboratory reporting limit of 0.008 mg/L as N (milligrams per liter as nitrogen). Therefore, it was assumed that most of the nitrite + nitrate reported by the laboratory is in the form of nitrate.

pH, and concentration of dissolved oxygen at 15-minute intervals. Periodic measurements of streamflow (per USGS techniques described by Carter and Davidian (1968) were made throughout the study period to develop a stage-discharge relation for the site that was used to compute continuous streamflow. Concentrations of nitrite + nitrate in water samples collected periodically from the site were compared to concurrent values of the flow and water-quality parameters measured on a continuous (15-minute interval) basis in an attempt to determine relations that can be used to predict the nitrite + nitrate load being carried by Bassett Creek.

The water samples were collected using standard USGS methods (Wilde and others, 1999), and analyzed for nitrite and nitrate at the USGS National Water-Quality Laboratory in Lakewood, Colorado. All laboratory methods are documented and verified for bias, accuracy, and precision with standard reference materials and participation in the USGS Office of Water Quality sample testing program (Pirkey and Glodt, 1998; Pritt and Raese, 1995). The concentration of nitrate in each sample was calculated as the difference between the laboratory-determined concentration of dissolved oxidized nitrite + nitrate and the corresponding concentration of nitrite in the same sample. Two field blanks were collected during the study period. In both field blanks, constituent concentrations were within acceptable limits, indicating that the results of the sample analyses were not affected by field or laboratory contamination.

Sampling and measurement of all parameters was conducted under both base-flow and stormflow conditions. Calculated streamflow and base flow, and the concentrations of nitrite + nitrate at base-flow and stormflow conditions that were associated with discrete water-quality samples collected during the study period, are shown in figure 2.

In order to place the information presented here in the proper context, it is important to note that although from a meteorological perspective water year 2003 was the wettest in the past decade according to the precipitation gage maintained by the NPS at Assateague Island (C. Zimmerman, NPS, written commun., 2005), the total annual streamflow volume as recorded by the Bassett Creek streamgaging station for that period was 88.9 million ft^3 (cubic feet), which was equivalent to 31.40 in. (inches) of precipitation over the watershed. In contrast, the total annual streamflow volume recorded during water year 2004 was 103.4 million ft^3, which was equivalent to 36.52 in. of precipitation over the watershed. The lower streamflow total for water year 2003 is the direct result of drought conditions in the region during 2002, which lowered the water level in the surficial aquifer and increased the tendency of precipitation to infiltrate the land surface and recharge the aquifer as opposed to flowing along the surface to the stream channel. Even though the Bassett Creek watershed received more precipitation during water year 2003 than it did during water year 2004, less water actually flowed down the stream channel.

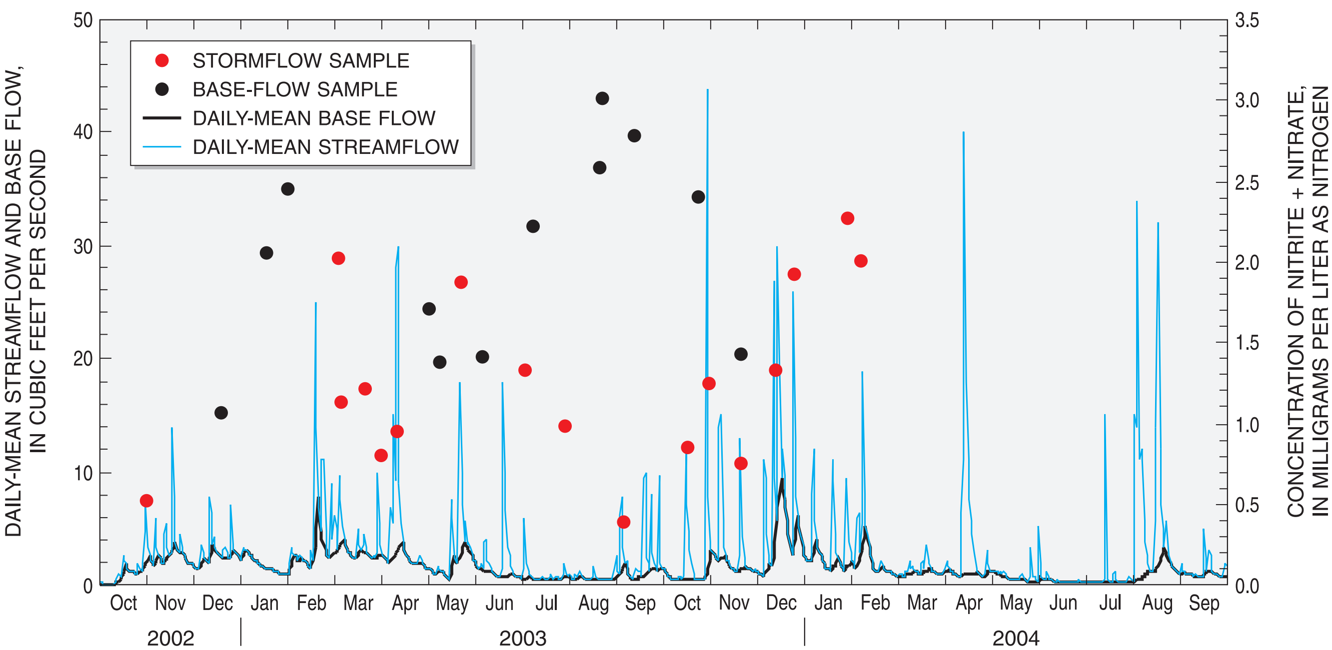

Figure 2. Streamflow, base flow, and concentrations of nitrite + nitrate at base flow and stormflow conditions in Bassett Creek near Ironshire, Maryland, water years 2003 and 2004.

Base Flow

Base flow is defined as sustained flow of a stream in the absence of direct runoff. Natural base flow is sustained largely by ground-water discharge (James and others, 2003). The magnitude of base flow varies seasonally with the elevation of the ground-water table, generally being larger during the winter and early spring when precipitation is high and plant transpiration is low, and lower during summer and early fall. Quantitative analysis of base flow over time is an interpretive exercise that can employ a number of different methods, and the accuracy of any result is open to debate. For the purposes of discrete sample collection for this study, however, streamflow at the study site was generally considered to consist solely of base flow when no measurable precipitation had fallen in the watershed within 3 days prior to sampling (R.W. James, Jr., USGS, oral commun., 2002).

Discharge

During the period October 2002 through September 2004, the lowest recorded instantaneous base flow of Bassett Creek was 0.06 ft^3/s (cubic feet per second), which occurred from October 3–10, 2002. The highest recorded base flow, 2.1 ft^3/s, occurred from January 2–4, 2004. Variations between these extremes followed the anticipated seasonal pattern. Daily values for the flows of Bassett Creek during the period can be found on pages 86 and 87 in James and others (2003) and on pages 102 and 103 in Saffer and others (2005).

Water Quality

During the study period, 12 discrete water samples were collected under base-flow conditions, at streamflows ranging between 0.52 ft^3/s and 1.6 ft^3/s. Laboratory analyses of these samples indicate concentrations of nitrite + nitrate ranging from 1.08 to 3.02 mg/L as N. The discrete concentrations of nitrite + nitrate were compared to concurrent values of flow and water-quality parameters measured on a continuous basis in an attempt to identify useful relations. The comparisons involved computation of Pearson's r, also called the linear correlation coefficient, and its associated significance statistic (Helsel and Hirsch, 1992). The square of the coefficient (R^2) is a measure of the proportion of the observed variation of a dependent variable that is explained by the value of the independent variable (Chatterjee and Price, 1977). This type of test assumes that the data being analyzed follow a normal distribution and have a constant variance. The significance statistic, or p-value, is the calculated probability, expressed in decimal form, that the relation described by the correlation coefficient is caused by random variation in the data. Thus, a small p-value indicates a high confidence that a relation does in fact exist.

Comparison of the laboratory-determined concentrations of nitrite + nitrate in the samples with other quantitative data collected concurrently with the samples shows that the concentration of nitrite + nitrate in the stream under base-flow conditions varied inversely with flow magnitude with R^2 = 0.90 and p = 0.0000. As explained above, these values of R^2 and p indicate that the magnitude of stream base flow explains 90 percent of the variation of nitrite + nitrate concentration in the discrete sample data, and that the statistical probability that there is a non-random relation between stream base flow and nitrite + nitrate concentration is greater than 99.99 percent. Figure 3 provides a graphic representation of the comparison.

A summary of all data collected at the site during the study period, including discrete concentrations of nitrite and nitrate, and daily values for water temperature, specific conductance, pH, and dissolved-oxygen concentration, can be found on pages 88–97 in James and others (2003) and on pages 104–112 in Saffer and others (2005). These data indicate that samples collected under base-flow conditions are characterized by nitrite concentrations that are more than two orders of magnitude smaller than nitrate concentrations in the corresponding samples. The data also indicate that total dissolved nitrogen concentrations range from 13 to 51 percent greater than concentrations of nitrite + nitrate in the corresponding samples, with mean and median differences being 34 and 37 percent greater, respectively.

Stormflow

Stormflow is streamflow caused by direct runoff of precipitation. Freeze and Cherry (1979) divide stormflow into two separate categories: overland flow, in which water travels over the land surface into the stream, and subsurface flow, in which water infiltrates the shallow subsurface as it flows to

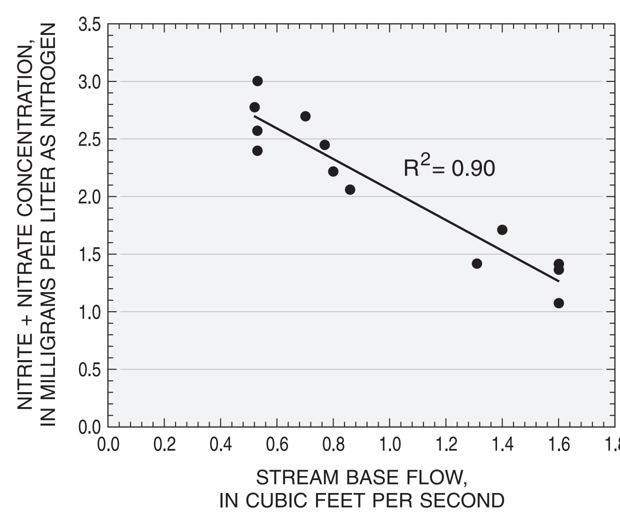

Figure 3. Concentrations of nitrite + nitrate during base-flow conditions at Bassett Creek near Ironshire, Maryland.

a seepage face in the stream bank and thus into the stream. The permeability of the surface soils in the study area make subsurface flow the dominant type of stormflow in the Bassett Creek watershed.

The magnitude of stormflow is highly variable and event-based, although the meteorological phenomena responsible for stormflow at the study site generally fall into two categories: cyclonic storms, usually occurring in late spring through early fall, and frontal storms, usually occurring from early fall through early spring. For the purposes of discrete-sample collection for this study, streamflow was generally considered to be dominated by stormflow if measurable precipitation had fallen within the watershed within 3 days prior to sampling (R.W. James, Jr., oral commun., 2002).

Discharge

During the period from October 2002 through September 2004, the highest recorded instantaneous peak associated with stormflow in Bassett Creek was 85 ft^3/s, which occurred on April 11, 2003. Many smaller stormflows also were recorded during the period. Information on additional stormflows and daily values for streamflow during the period can be found on pages 86 and 87 in James and others (2003) and on pages 102 and 103 in Saffer and others (2005).

Water Quality

During the study period, 17 discrete water samples were collected under stormflow conditions (1.9 ft^3/s to 84 ft^3/s) and analyzed to determine nutrient species concentrations. The results of these analyses show concentrations of nitrite + nitrate ranging from 0.397 mg/L as N to 2.28 mg/L as N. Comparison of these data with other quantitative data collected concurrently with the samples shows that the concentration of nitrite + nitrate in the stream under stormflow conditions has no statistically significant relation to flow magnitude (fig. 4). Additional analyses did indicate a statistically significant relation between stormflow concentrations of nitrite + nitrate and water temperature. This relation may reflect the seasonal availability of nitrite + nitrate as it is affected by agricultural practices in the watershed, but the correlation between the variables ($R^2 = 0.25$, $p = 0.0497$) is not strong enough to be used for estimation of nutrient loads.

A summary of all data collected at the Bassett Creek site during the study period, including discrete concentrations of nitrite and nitrate, and daily values for water temperature, specific conductance, pH, and dissolved-oxygen concentration, can be found on pages 86–97 in James and others (2003) and on pages 102–112 in Saffer and others (2005). These data indicate that samples collected under stormflow conditions are characterized by nitrite concentrations that are primarily more than two orders of magnitude smaller than nitrate concentrations in the corresponding samples (three storm samples had nitrite concentrations that comprised between 1 and 3 percent of the sample nitrite + nitrate concentration). The data also indicate that concentrations of total dissolved nitrogen range between 16 and 307 percent greater than concentrations of nitrite + nitrate in the corresponding samples, with mean and median differences being 114 and 116 percent greater, respectively. These differences were caused primarily by greater amounts of dissolved organic nitrogen in storm samples.

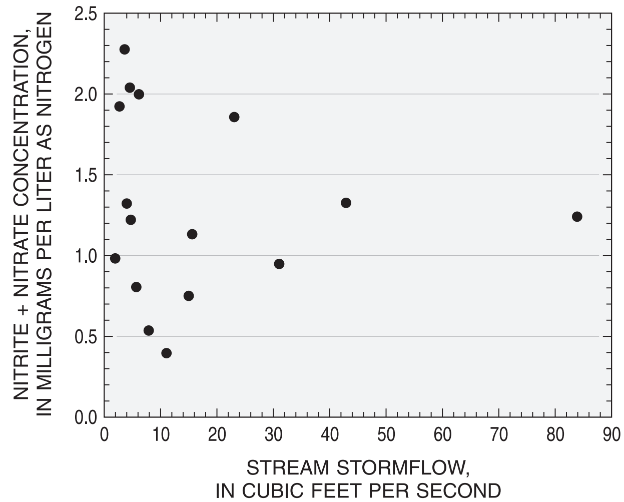

Figure 4. Concentrations of nitrite + nitrate during stormflow conditions at Bassett Creek near Ironshire, Maryland.

Estimated Load of Nitrite + Nitrate

In the context of this report, a load refers to a mass of constituent that is delivered in a specified time period. In particular, this report is concerned with the load of nitrite + nitrate carried by the nontidal part of Bassett Creek toward the MD Coastal Bays during water years 2003 and 2004. Loads of nitrite + nitrate for the study period were estimated by using the log-linear regression model ESTIMATOR (Cohn and others, 1989). ESTIMATOR computes loads in two steps. First, a center-estimate linear model is fit to the logarithms of the concentration using ordinary least-squares regression. The model uses the Minimum Variance Unbiased Estimator (MVUE) developed by Bradu and Mundlak (1970) to correct for bias when transforming data from logarithmic space to arithmetic space. The Adjusted Maximum Likelihood Estimator (AMLE) (Cohn, 1988) is used to estimate the log-linear model for sites having censored observations, which are concentration values below a detectable limit.

Separate models were constructed for total nitrite + nitrate load (using the calculated daily-mean streamflows and concentrations of nitrite + nitrate from all discrete water-quality samples collected during the study), and base-flow nitrite + nitrate load (using base-flow estimates from the PART program (Rutledge, 1998) and the concentrations of nitrite + nitrate from discrete water-quality samples collected during base-flow conditions; see fig. 2). Each regression model is of the form:

$$\ln(c) = \beta_0 + \beta_1 \ln(q/\tilde{Q}) + \beta_2(t - \tilde{T}) + \varepsilon \qquad (1)$$

where

- c is concentration,
- q is mean-daily streamflow,
- t is time,
- $\tilde{Q}$ and $\tilde{T}$ are centering values for streamflow and time, respectively,
- β_i are the estimated coefficients of the regression ($i = 0, 1, 2$),

and

- ε is residual error.

Although ESTIMATOR may use as many as seven predictor variables, in this study, the small number of observations (only 12 for the base-flow load model) allowed the use of a maximum of two predictor variables.

The models that resulted provide a reasonable fit to the data, with R^2 values of 0.83 and 0.84 for concentration and load, respectively, in the base-flow load model, and 0.40 and 0.88 for concentration and load, respectively, in the total load model. The model mean-square errors are 0.38 for base-flow load and 0.64 for total load.

There are several concerns regarding the use of the statistical regression model employed by ESTIMATOR for load estimation in this study. As a result of these concerns, errors reported for the estimated loads (based on the fit of the model to the observations) may not equal the true errors (difference between estimated and true loads).

The first concern has to do with the sample size. For this study, the sample size is 29 for the total load model and 12 for the base-flow load model. ESTIMATOR typically performs best with at least 25 samples per year, with half at high flow and half uniformly distributed over the course of the year, and a minimum of 3 years of sampling.

A second concern is with the small size of the basin and the correspondingly short time-scales for variation in streamflow and chemical concentration. The model is conditioned on mean-daily streamflow, so it is assumed that the measured concentration is representative of that particular day. If either or both streamflow and chemical concentration vary over the course of the day, this assumption will likely not be met, thereby introducing additional error. The approach taken in ESTIMATOR is best suited for basins with areas greater than 100 mi^2 (Cohn, 1995); application to smaller basins may introduce bias. In smaller basins, stratified sampling or statistically based sampling methods (Thomas, 1985) have proven useful, especially for estimating sediment loads, but require a different sampling strategy than the one used by this project.

A third concern is with extrapolation of the model for load estimation beyond the period of water-quality sample collection. Sampling was conducted throughout water year 2003, but for only a part of water year 2004 (October through February). Loads were estimated for both the 2003 and 2004 water years, conditioned on measured streamflow for the period, but on water-quality data collected for less than the entire period. One result of this extrapolation is that the estimated standard errors and confidence intervals are larger for the period March through September 2004 than for the period October 2003 through February 2004.

With these concerns in mind, the estimated nitrite + nitrate loading rate for water year 2003 was 9.3 kg/d (kilograms per day) (total load of 3,400 kilograms per year or 7,500 pounds per year). In water year 2004, the estimated nitrite + nitrate loading rate was 13.9 kg/d (total load of 5,100 kilograms per year or 11,200 pounds per year). The base-flow component of the estimated nitrite + nitrate load comprised approximately 61 percent and 24 percent of the total estimated nitrite + nitrate load in water years 2003 and 2004, respectively. The total estimated monthly nitrite + nitrate loading rate ranged from 3.9 kg/d to 31.1 kg/d, while the base-flow components of the estimated monthly nitrite + nitrate loading rate ranged from 1.8 kg/d to 7.8 kg/d (fig. 5).

In figure 5, the estimated monthly loads of nitrite + nitrate are shown as bars representing the best estimate of the monthly base-flow and total loads. Monthly storm loads can be inferred by comparing base-flow and total loads. The error bars in figure 5 indicate the 95-percent confidence interval, calculated from the standard error of prediction of nitrite + nitrate load.

Over the study period, a seasonal pattern of monthly nitrite + nitrate loading was observed, with both stormflow and total estimated loads of nitrite + nitrate increasing during the late winter and spring months. In water year 2003, most of the estimated nitrite + nitrate load during the late summer, fall, and early winter was transported in base flow, although fall storms resulted in significant stormflow loads, as occurred in September 2003 and the late summer and fall of 2004.

Base-flow loads of nitrite + nitrate were generally lower in water year 2004 (approximately 2,700 pounds as nitrogen) than in 2003 (approximately 4,700 pounds as nitrogen), despite higher overall total streamflow. The increased loading in water year 2004 (estimated loads of nitrite + nitrate were almost 50 percent higher in water year 2004 than in water year 2003) generally comes from stormflow.

Although different watersheds in the coastal bays drainage have somewhat different characteristics, it is nevertheless interesting to compare the estimated annual base-flow loads mentioned above with the results presented in Dillow and Greene (1999). In that study, an average annual stream base-flow load estimate was presented for the entire coastal bays drainage. Applying that estimate to the Bassett Creek watershed leads to an estimated annual base-flow nitrate

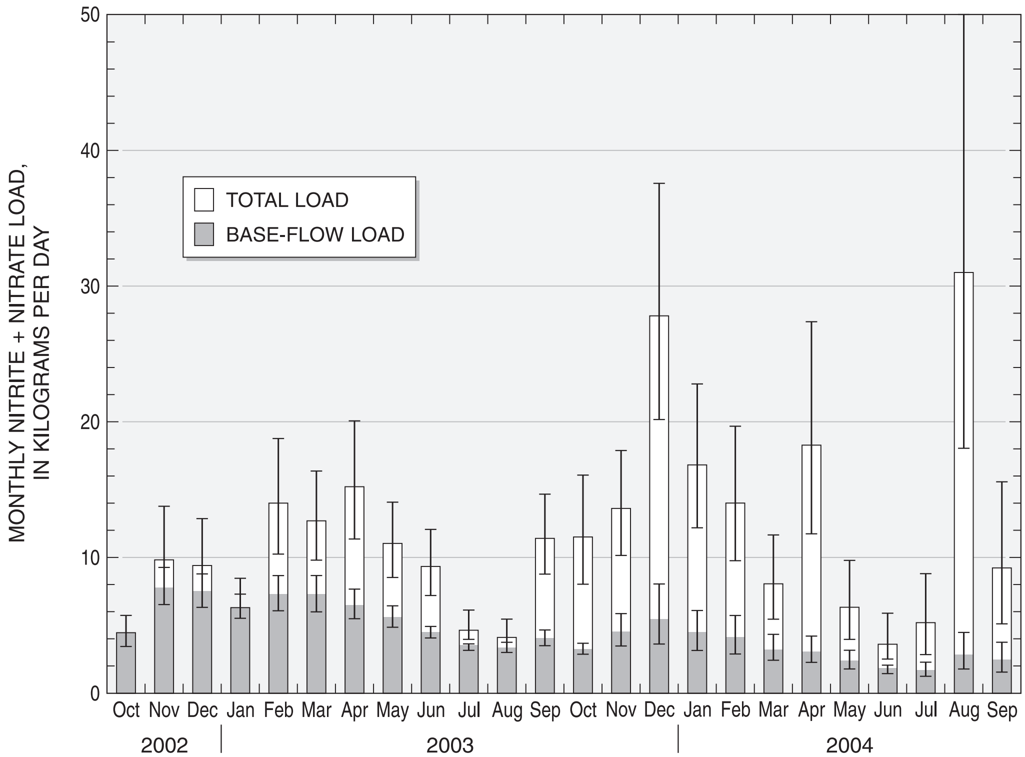

Figure 5. Monthly loads of nitrite + nitrate at Bassett Creek near Ironshire, Maryland, water years 2003 and 2004. (Error bars indicate the 95-percent confidence interval.)

Table 1. Calculated flow-weighted concentrations of nitrite + nitrate for three sites in the Coastal Plain of Maryland.

[WY, water year; CY, calendar year; values for Chesterville Branch (station number 01493112) are based on results from the study described by Senus and others (2005), in which loads of nitrite + nitrate were calculated, but not reported (M.P. Senus, USGS, written commun., 2005). For Choptank River (station number 01491000), values were calculated from loads reported on the River Input Monitoring web site at http://va.water.usgs.gov/chesbay/RIMP/index.html.]

Station name	USGS station number	Sampling period	Flow-weighted concentration, nitrite + nitrate, in milligrams per liter as nitrogen		
			Minimum	Maximum	Mean
Bassett Creek near Ironshire, MD	01484719	WY 2003–2004	1.35	1.74	1.54
Chesterville Branch near Crumpton, MD	01493112	CY 1997–2001	4.21	6.71	5.37
Choptank River near Greensboro, MD	01491000	CY 1985–2004	0.95	1.30	1.09

load of approximately 1,500 pounds per year as nitrogen. This indicates that base-flow nitrate loads from Bassett Creek may be 2 to 3 times larger than the average load calculated in the earlier study.

A flow-weighted concentration may be calculated as the annual load divided by the annual streamflow. For water years 2003 and 2004, the flow-weighted concentrations of nitrite + nitrate for Bassett Creek are 1.35 mg/L as N and 1.74 mg/L as N, respectively. Although load estimates made by using similar methods are not available for other coastal bays sites, flow-weighted concentrations are calculated based on information on loads of nitrite + nitrate from two other Coastal Plain sites (Chesterville Branch near Crumpton, MD, and Choptank River near Greensboro, MD) (table 1). The flow-weighted concentrations of nitrite + nitrate for Bassett Creek are similar to the maximum value for the period spanning calendar years 1985 through 2004 for the Choptank River (1.30 mg/L as N), and lower than the range of values for calendar years 1997 through 2001 for Chesterville Branch (4.21 mg/L as N to 6.71 mg/L as N).

Senus and others (2005) noted higher yields (load divided by area) of total nitrogen for Chesterville Branch than for the Choptank River. That study also described a positive correlation between total nitrogen yield and percentage of agricultural land use in several basins in the Chesapeake Bay watershed. Forty-eight percent of the gaged part of the Bassett Creek watershed is characterized by agricultural land use; this proportion is similar to the land-use characterization of the Choptank River watershed (50 percent agricultural), and much less than that of the Chesterville Branch watershed (92 percent agricultural).

Summary and Conclusions

In recent years, the National Park Service and the U.S. Geological Survey have been partnering on a series of studies to understand the potential for streams and ground water in the tributary watersheds to contribute excess nutrients to the MD Coastal Bays. The study site on Bassett Creek near Ironshire, MD, carries streamflow from a 1.22-square-mile, nontidal watershed. The results of streamflow and water-quality monitoring and sampling at the site from October 2002 through September 2004 were used to draw several conclusions regarding concentrations and loads of nitrite + nitrate that are characteristic of the site during the period.

Concentrations of nitrite + nitrate in water samples collected at the site (at streamflows between 0.52 cubic feet per second and 84 cubic feet per second) ranged from 0.397 milligrams per liter as nitrogen to 3.02 milligrams per liter as nitrogen, routinely exceeding the established threshold (0.4 milligrams per liter as nitrogen) that indicates anthropogenic effects. According to these criteria, concentrations of nitrite + nitrate in the study watershed are being affected by human activities.

Concentrations of nitrite + nitrate in water samples collected during base-flow conditions have a strong ($R^2 = 0.90$), statistically significant relation with streamflow magnitude, with greater concentrations being associated with lesser streamflows, implying a dilution relation with the nitrite + nitrate source(s). Concentrations of nitrite + nitrate in water samples collected during stormflow conditions have a weak ($R^2 = 0.25$), statistically significant relation with water temperature that may indicate some seasonal variation in concentrations of nitrite + nitrate in the watershed. Sixty-one percent and 24 percent of the estimated load of nitrite + nitrate during water years 2003 and 2004, respectively, was transported in base flow. These base-flow loads are 2 to 3 times larger than the average base-flow load estimated in an earlier U.S. Geological Survey study of ground-water discharge and nitrate loadings to the coastal bays of Maryland.

The average loads of nitrite + nitrate carried from the watershed by Bassett Creek are estimated to have been 9.3 kilograms per day during water year 2003 and 13.9 kilograms per day during water year 2004. The estimated monthly total nitrite + nitrate loading rate ranged from 3.9 kilograms per day to 31.1 kilograms per day, whereas the estimated monthly base-flow nitrite + nitrate loading rate ranged from 1.8 kilograms per day to 7.8 kilograms per day.

The flow-weighted concentrations of nitrite + nitrate for Bassett Creek during water years 2003 (1.35 milligrams per liter as nitrogen) and 2004 (1.74 milligrams per liter as nitrogen) are similar to the maximum value for the period spanning calendar years 1985 through 2004 for the Choptank River near Greensboro, MD (1.30 milligrams per liter as nitrogen), and lower than the range of values for calendar years 1997 through 2001 for Chesterville Branch near Crumpton, MD (4.21 milligrams per liter as nitrogen to 6.71 milligrams per liter as nitrogen). These comparative values may reflect the effect of the areal extent of agricultural land use in the respective watersheds.

Acknowledgments

The authors wish to thank Brian Sturgis and Alex Almario of the Natural Resource Management Division of the National Park Service at Assateague Island National Seashore for their assistance in stormwater-quality sample collection, and in performing basic field maintenance on the continuous water-quality sensors to minimize interruptions in data collection.

References Cited

Bachman, L.J., and Phillips, P.J., 1996, Hydrologic landscapes on the Delmarva Peninsula, part 2—Estimates of base-flow nitrogen load to Chesapeake Bay: Water Resources Bulletin, v. 32, no. 4, p. 779–791.

Blazer, V.S., Phillips, S.W., and Pendleton, E.C., 1998, Fish health, fungal infections, and *Pfiesteria*: The role of the U.S. Geological Survey: U.S. Geological Survey Fact Sheet FS-114-98, 4 p.

Bradu, D., and Mundlak, Y., 1970, Estimation in log-normal linear models: Journal of the American Statistical Association, v. 65, no. 329, p. 198–211.

Carter, R.W., and Davidian, Jacob, 1968, General procedure for gaging streams: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A6, 13 p.

Chatterjee, Samprit, and Price, Bertram, 1977, Regression analysis by example: New York, NY, John Wiley, 228 p.

Cohn, T.A., 1988, Adjusted maximum likelihood estimation of the moments of lognormal populations from type 1 censored samples: U.S. Geological Survey Open-File Report 88–350, 34 p.

Cohn, T.A., 1995, Recent advances in statistical methods for the estimation of sediment and nutrient transport in rivers: Reviews of Geophysics, Supplement to Volume 33, p. 1,117–1,123.

Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., and Summers, R.M., 1992, The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research, v. 28, no. 9, p. 2,353–2,363.

Cohn, T.A., DeLong, L.L., Gilroy, E.J., Hirsch, R.M., and Wells, D.K., 1989, Estimating constituent loads: Water Resources Research, v. 25, no. 5, p. 937–942.

Dillow, J.J.A., Banks, W.S.L., and Smigaj, M.J., 2002, Ground-water quality and discharge to Chincoteague and Sinepuxent Bays adjacent to Assateague Island National Seashore, Maryland: U.S. Geological Survey Water-Resources Investigations Report 02–4029, 42 p.

Dillow, J.J.A., and Greene, E.A., 1999, Ground-water discharge and nitrate loadings to the Coastal Bays of Maryland: U.S. Geological Survey Water-Resources Investigations Report 99–4167, 8 p.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, NJ, Prentice Hall, 604 p.

Hamilton, P.A., Denver, J.M., Phillips, P.J., and Shedlock, R.J., 1993, Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia—Effects of agricultural activities on nitrate and inorganic constituents in the surficial aquifer: U.S. Geological Survey Open-File Report 93–40, 87 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: Amsterdam, Elsevier Science Publishers, 522 p.

James, R.W., Jr., Saffer, R.W., Pentz, R.H., and Tallman, A.J., 2003, Water resources data, Maryland and Delaware, water year 2003, volume 1—Surface-water data: U.S. Geological Survey Water-Data Report MD-DE-DC-03-1, 522 p. Also available on the World Wide Web, accessed December 1, 2005, at URL *http://pubs.usgs.gov/wdr/wdr-md-de-dc-03-1/pdf/wdr-md-de-dc-03-1.pdf*

Maryland Department of the Environment, 1993, Maryland's Coastal Bays: An assessment of aquatic ecosystems, pollutant loadings, and management options: Baltimore, Maryland, Chesapeake Bay and Special Projects Branch, Maryland Department of the Environment, 46 p.

National Oceanic and Atmospheric Administration, 1990, A Special NOAA 20th anniversary report—Estuaries of the United States: Vital statistics of a national resource base: Rockville, Maryland, Strategic Assessment Branch, Ocean Assessments Division, Office of Oceanography and Marine Assessment, National Ocean Service, National Oceanic and Atmospheric Administration, 79 p.

Pirkey, K.D., and Glodt, S.R., 1998, Quality control at the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Fact Sheet FS-026-98, 4 p.

Pritt, J.W., and Raese, J.W., 1995, Quality assurance/quality control manual—National Water Quality Laboratory: U.S. Geological Survey Open-File Report 95–443, 35 p.

Rutledge, A.T., 1998, Computer programs for describing the recession of ground-water discharge and for estimating mean ground-water recharge and discharge from streamflow data—update: U.S. Geological Survey Water-Resources Investigations Report 98–4148, 43 p.

Saffer, R.W., Pentz, R.H., and Tallman, A.J., 2005, Water resources data, Maryland, Delaware and Washington, D.C., water year 2004, volume 1—Surface-water data: U.S. Geological Survey Water-Data Report MD-DE-DC-04-1, 574 p. Also available on the World Wide Web, accessed December 1, 2005, at URL *http://pubs.usgs.gov/wdr/2004/wdr-md-de-dc-04-1/*

Senus, M.P., Langland, M.J., and Moyer, D.L., 2005, Nutrient and sediment concentrations, loads, and trends for four nontidal tributaries in the Chesapeake Bay Watershed, 1997–2001: U.S. Geological Survey Scientific Investigations Report 2004–5125, 33 p.

Shedlock, R.J., Denver, J.M., Hayes, M.A., Hamilton, P.A., Koterba, M.J., Bachman, L.J., Phillips, P.J., and Banks, W.S.L., 1999, Water quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia: Results of investigations, 1987–91: U.S. Geological Survey Water-Supply Paper 2355-A, 41 p.

Thomas, R.B., 1985, Estimating total suspended sediment yield with probability sampling: Water Resources Research, v. 21, no. 9, p. 1,381–1,388.

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., 1999, National field manual for the collection of water-quality data—Collection of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, 156 p.

Prepared by the Maryland-Delaware-District of Columbia
Water Science Center's Publishing Service Center 3.
Edited by Valerie M. Gaine.
Graphics by Timothy W. Auer.
Layout by Ann Marie Squillacci (Publishing Service Center 1).

For additional information, contact:
Director, MD-DE-DC Water Science Center
U.S. Geological Survey
8987 Yellow Brick Road
Baltimore, MD 21237

or visit our Web site at:
http://md.water.usgs.gov

Dillow, J.J.A., Raffensperger, J.P.—**Estimates of the Loads of Nitrite + Nitrate in the Flow of Bassett Creek to the Maryland Coastal Bays Adjacent to Assateague Island National Seashore, Water Years 2003–2004**—U.S. Geological Survey Scientific Investigations Report 2006–5080