Sources, Fate, and Transport of Nitrogen and Phosphorus in the Chesapeake Bay Watershed: An Empirical Model

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

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Conversion Factors

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km^2)	247	acre
hectare (ha)	0.003861	square mile (mi^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
cubic meter (m^3)	35.3	cubic foot (ft^3)
	Mass	
kilogram (kg)	2.205	pound, avoirdupois (lb)
megagram (Mg)	1.102	ton, short (2,000 lb)
kilogram per square kilometer (kg km^{-2})	0.00892	pound per acre (lb $acre^{-1}$)

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

$$°F = (1.8 \times °C) + 32$$

For units of measurement, this text uses negative exponents instead of the more common "per" symbol (/). As examples, m yr^{-1} herein is equivalent to m/yr (meters per year), and kg km^{-2} herein is equivalent to kg/km^2 (kilograms per square kilometer).

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Abstract

Spatially Referenced Regression on Watershed Attributes (SPARROW) was used to provide empirical estimates of the sources, fate, and transport of total nitrogen (TN) and total phosphorus (TP) in the Chesapeake Bay watershed, and the mean annual TN and TP flux to the bay and in each of 80,579 nontidal tributary stream reaches. Restoration efforts in recent decades have been insufficient to meet established standards for water quality and ecological conditions in Chesapeake Bay. The bay watershed includes 166,000 square kilometers of mixed land uses, multiple nutrient sources, and variable hydrogeologic, soil, and weather conditions, and bay restoration is complicated by the multitude of nutrient sources and complex interacting factors affecting the occurrence, fate, and transport of nitrogen and phosphorus from source areas to streams and the estuary. Effective and efficient nutrient management at the regional scale in support of Chesapeake Bay restoration requires a comprehensive understanding of the sources, fate, and transport of nitrogen and phosphorus in the watershed, which is only available through regional models. The current models, Chesapeake Bay nutrient SPARROW models, version 4 (CBTN_v4 and CBTP_v4), were constructed at a finer spatial resolution than previous SPARROW models for the Chesapeake Bay watershed (versions 1, 2, and 3), and include an updated timeframe and modified sources and other explanatory terms.

Chesapeake Bay receives an estimated 1.32×10^8 kilograms (132,000 metric tons) of nitrogen and 9.74×10^6 kilograms (9,740 metric tons) of phosphorus annually from its watershed, mainly through its two largest tributaries, the Susquehanna and Potomac Rivers. Significant (α=0.10) sources of nutrients to streams in the watershed include fertilizer and manure applications in agricultural areas, undifferentiated urban activities, point sources, atmospheric deposition and direct fixation by crops (for nitrogen), and mineral sources (for phosphorus). Agriculture (primarily fertilizer applications and crop fixation) contributes more than half of the nitrogen delivered from the watershed to the bay; phosphorus contributions are more mixed, and fairly evenly distributed among agricultural (fertilizer and manure applications) and urban (including point) sources. Natural mineral dissolution contributes approximately 14 percent of the phosphorus flux from the watershed to the Chesapeake Bay. Empirical estimates of average yields from different source areas and of the portion of selected applications delivered to streams agree closely with previously reported values in the literature.

Nutrient fate and transport through the Chesapeake Bay watershed to the bay reflect the different physical and chemical properties of nitrogen and phosphorus compounds. Groundwater is an important pathway for nitrogen transport (as nitrate), and TN flux is greatest in areas with greater groundwater flow and in areas of the Piedmont underlain by carbonate rocks. TN flux decreases with increasing vegetative growth (likely indicative of plant uptake) and soil available water capacity (likely indicative of reducing conditions). Phosphorus transport to streams, conversely, is greatest in areas most likely to generate overland runoff and related erosion, including those with less permeable and more erodible soils and greater precipitation. Phosphorus transport also is greater in the Coastal Plain than in other areas, possibly due to saturation of soils with historical phosphorus applications. Both nitrogen and phosphorus are lost within watershed impoundments (lakes, ponds, or reservoirs), and nitrogen is also lost significantly along flowing reaches, particularly in small streams and in larger streams in warmer areas.

Introduction

Chesapeake Bay has been the focus of water-quality and ecological restoration efforts for several decades (Phillips, 2007; U.S. Environmental Protection Agency, 2008). As the largest and most productive estuary in North America (U.S. Environmental Protection Agency, 2008), the bay is a vital ecological and economic resource. The bay and its tributaries have been degraded in recent decades, however, by excessive nutrients (nitrogen and phosphorus) and sediment from contributing watersheds. In 2000, the bay was listed as "impaired" under the Clean Water Act (Langland and others, 2003). Terrestrial and atmospheric inputs to Chesapeake Bay have increased by a factor of 6 to 8 for nitrogen and 13 to 24 for phosphorus since European colonization (Boynton and others, 1995). Impacts of excessive nutrients and sediment include algal blooms, increased turbidity, decreased abundance of submerged aquatic vegetation and dissolved oxygen, and declining fisheries (Kemp and others, 2005; U.S. Environmental Protection Agency, 2008). Only 12 percent of Chesapeake tidal waters met ecological criteria for dissolved-oxygen levels during the summer months of 2005, 2006, and 2007, and only 26 percent had acceptable chlorophyll-*a* levels in 2007 (U.S. Environmental Protection Agency, 2008). Although primary production in temperate estuaries is often nitrogen-limited (Vitousek and others, 1997), concentrations of nutrients and chlorophyll from 1985 through 2008 suggest that both nitrogen and phosphorus may limit production in Chesapeake Bay during different seasons and that phosphorus is the limiting nutrient in the spring (Prasad and others, 2010). Chesapeake Bay restoration efforts have been coordinated and managed since the 1980s by the U.S. Environmental Protection Agency (USEPA) in cooperation with other Federal, State, and local agencies through the Chesapeake Bay Program; current efforts are focused on pollution reduction, habitat restoration, fisheries management, watershed protection, and fostering public stewardship (U.S. Environmental Protection Agency, 2008).

Restoration efforts in the Chesapeake Bay watershed in recent decades have been insufficient to meet established standards. Concentrations of nitrogen and phosphorus in the estuary generally decreased between 1985 and 2008, and are controlled primarily by inputs from tributaries, which generally peaked in 1997 and have decreased since 2004 (Prasad and others, 2010). Natural variability in streamflow significantly affects fluvial nutrient fluxes, however. When adjusted for streamflow, trends from 1985 through 2008 are generally negative for nitrogen and phosphorus in most Chesapeake tributaries, although fluxes have increased in some streams (U.S. Geological Survey, 2009). Increasing nitrogen flux in the Choptank River, for example, likely reflects the importance of groundwater to nitrogen transport and increasing nitrate in groundwater in areas of the Delmarva Peninsula (Debrewer and others, 2008; Hirsch and others, 2010). In spite of generally decreasing nutrient fluxes in Chesapeake tributaries and concentrations in the estuary, concentrations are not decreasing quickly enough to meet established water-quality standards and the bay remains degraded (U.S. Environmental Protection Agency, 2008). Total maximum daily loads (TMDLs) have been established for nitrogen and phosphorus in the Chesapeake Bay to help manage nutrient reductions as mandated by the Clean Water Act (U.S. Environmental Protection Agency, 2011), and Presidential Executive Order 13508 of 2009 directed multiple Federal agencies to develop and implement a new strategy for Chesapeake Bay protection and restoration (Federal Leadership Committee for Chesapeake Bay, 2010).

Chesapeake Bay restoration is complicated by the multitude of nutrient sources and complex interacting factors affecting the occurrence, fate, and transport of nitrogen and phosphorus from source areas to streams and the estuary. Chesapeake Bay drains 166,000 km^2 (square kilometers) in six states and the District of Columbia (fig. 1). Most of the watershed is forested, but intensive agriculture and urban development occur in many areas. Major sources of nutrients to the bay and its tributaries include wastewater treatment plants, fertilizer and manure applications, and (for nitrogen) atmospheric deposition (Preston and Brakebill, 1999; Moore and others, 2011). Natural hydrologic, geologic (fig. 2), and soil conditions relevant to the movement and persistence of nitrogen and phosphorus in the environment are also variable within the bay watershed. Nitrogen is readily transported as nitrate to groundwater and streams in areas underlain by carbonate bedrock (Ator and Ferrari, 1997; Miller and others, 1997; Ator and others, 1998; Lindsey and others, 1998; Greene and others, 2005) and in areas of the Coastal Plain with well-drained permeable soils and sediments and oxic groundwater (Ator and others, 2005; Denver and others, 2010). Nitrate transported through groundwater contributes nearly half of the nitrogen flux in Chesapeake tributaries (Phillips and others, 1999). Multidecadal traveltimes typical of groundwater significantly complicate the understanding of restoration effectiveness, however, particularly when delays due to slow groundwater flow exceed the period of monitoring record. Phosphorus is less soluble than nitrate and is consequently transported most effectively in areas with steep slopes and (or) impermeable soils and sediments where overland runoff of precipitation is most likely. The design of restoration and management practices to mitigate nutrient transport is particularly complicated by the variety of these interacting natural factors (for example, Kaushal and others, 2008).

Effective and efficient nutrient management at the regional scale in support of Chesapeake Bay restoration requires a comprehensive understanding of the sources, fate, and transport of nitrogen and phosphorus in the watershed that is available only through regional models. Targeting limited restoration and management resources most effectively requires an understanding of the spatial distribution and relative magnitude of nutrient sources (Castro and others, 2003), the natural conditions affecting nutrient fate and transport, and the most vulnerable or valuable resources to be protected.

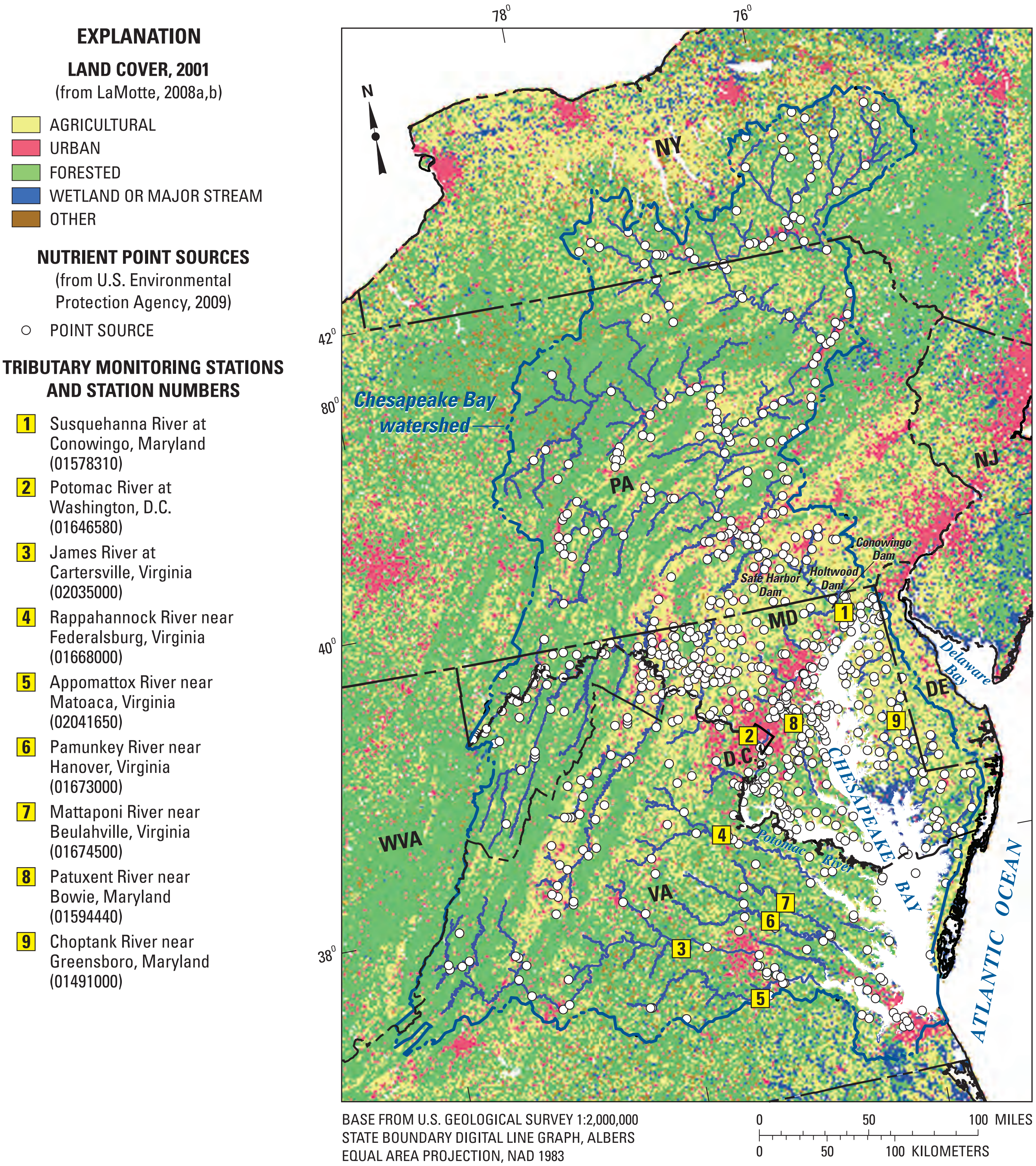

Figure 1. Location of the Chesapeake Bay watershed and vicinity, including generalized land cover, point sources, and selected long-term stream monitoring stations for nutrient flux.

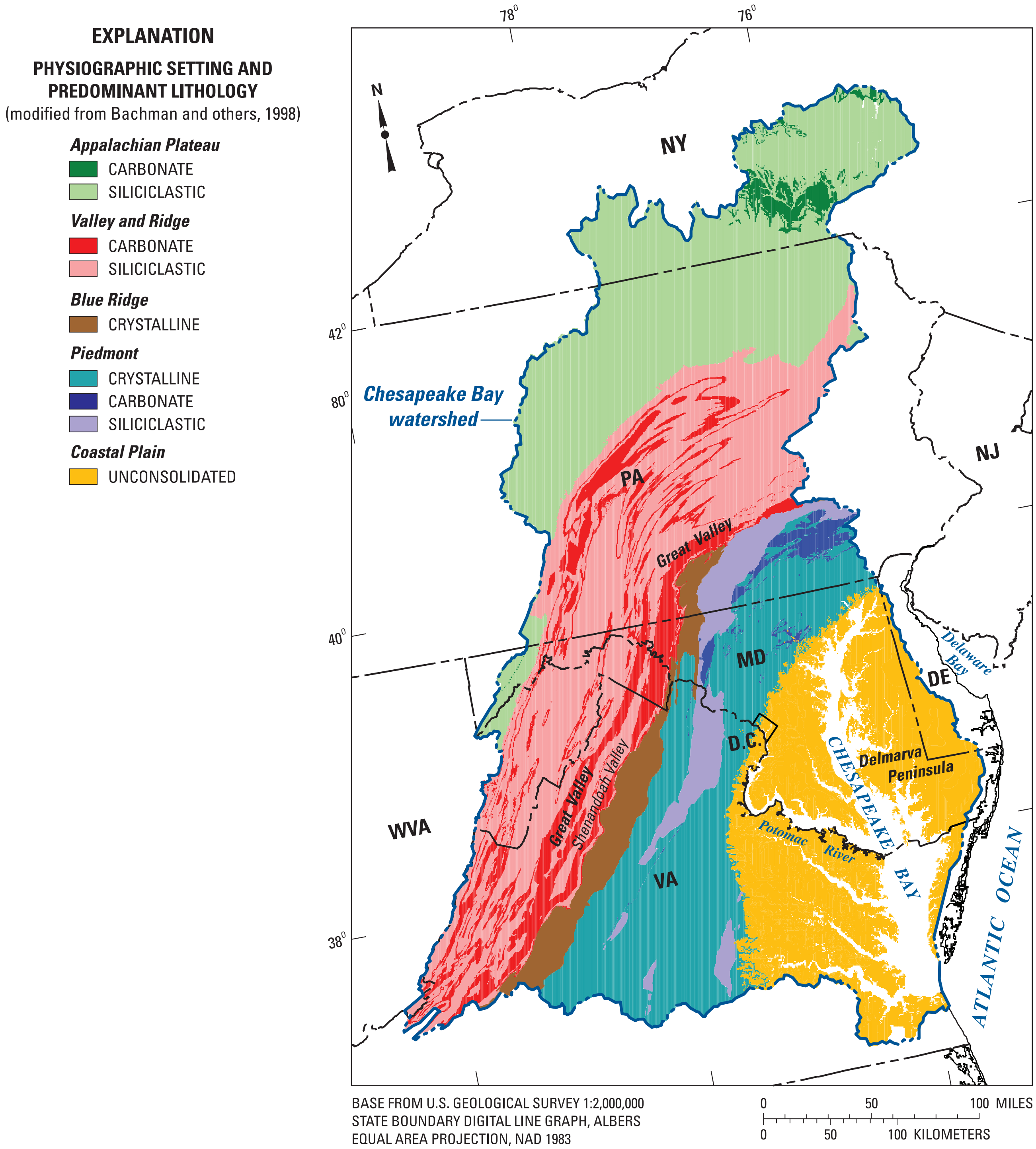

Figure 2. Hydrogeologic settings within the Chesapeake Bay watershed.

Available research on nutrients in the watershed supports conceptual models of these factors; however, consistent, comprehensive, and quantitative estimates require the use of numerical models. Spatially Referenced Regression On Watershed attributes (SPARROW) (Schwarz and others, 2006; Preston and others, 2009) has been used to estimate the total flux of nitrogen and phosphorus to Chesapeake Bay from the watershed and quantify nutrient sources and factors affecting the fate and transport for the late 1980s and early and late 1990s (Preston and Brakebill, 1999; Brakebill and others, 2001; Brakebill and Preston, 2004). Similar SPARROW models have also been calibrated for the wider northeastern United States (Moore and others, 2011), the upper Mississippi River watershed (Alexander and others, 2008), and the continental United States (Smith and others, 1997). Hydrological Simulation Program–FORTRAN (HSPF) (Bicknell and others, 1996) has also been used extensively to understand nutrient and sediment sources, fate, and transport in support of Chesapeake Bay restoration (U.S. Environmental Protection Agency, 1998). Other models that have been applied to evaluate nutrients in areas of the Chesapeake Bay watershed include MODFLOW (Sanford and Pope, 2011) and SWAT (Meng and others, 2010).

Purpose and Scope

The sources, fate, transport, and flux of total nitrogen (TN) and total phosphorus (TP) in the Chesapeake Bay watershed are presented and discussed in this report. Interpretations are based on SPARROW models calibrated to mean annual conditions in 2002 in the Chesapeake Bay watershed for TN and TP. These models, CBTN_v4 and CBTP_v4, were constructed at a finer spatial resolution than previous SPARROW models for the Chesapeake Bay watershed (versions 1, 2, and 3; Preston and Brakebill, 1999; Brakebill and others, 2001; Brakebill and Preston, 2004), and include an updated timeframe and modified sources and other explanatory terms. The development and calibration of the models are presented and discussed, along with the estimated flux of nitrogen and phosphorus in major tributaries and to the bay, the spatial distribution and significance of major sources, and significant factors affecting nitrogen and phosphorus delivery to stream channels and in-stream fate and transport. Specific estimates of nitrogen and phosphorus fluxes for each of 80,579 nontidal stream reaches within the watershed also are presented, including the total flux in each reach and the local (incremental) flux contributed by the local watershed and independent of any upstream contributions. This report is intended primarily for watershed managers and others needing a comprehensive, quantitative, and spatially distributed accounting and understanding of nitrogen and phosphorus in the Chesapeake Bay watershed; those seeking a detailed discussion of the theory, development, and application of SPARROW modeling are referred to Smith and others (1997) and Schwarz and others (2006).

Methods

The SPARROW modeling approach (Smith and others, 1997; Schwarz and others, 2006) was used to estimate the mean annual flux of TN and TP to Chesapeake Bay and in each of 80,579 nontidal tributary reaches, and to identify and quantify significant factors affecting the occurrence, fate, and transport of nitrogen and phosphorus in streams of the bay watershed. SPARROW is a spatially explicit, mass-balance watershed model that uses nonlinear regression to quantify the spatial relation between observed constituent (such as nitrogen or phosphorus) fluxes in nontidal streams (the response or dependent variable) and constituent sources and factors affecting their overland and in-stream fate and transport (the explanatory or independent variables). Annual nutrient fluxes used as response variables to calibrate the models were estimated from observed streamflow and water chemistry on monitored streams. Response and explanatory variables were geographically referenced to a digital network of stream reaches and associated watershed catchments that facilitates the routing of water and associated constituents throughout the landscape. The SPARROW models predict the long-term mean-annual TN and TP flux for each network stream reach as a function of sources, factors influencing non-conservative delivery to the stream channel, and in-stream fate and transport. Mass-balance constraints ensure the in-stream nutrient flux at the end of each model reach equals the sum of flux generated within the reach subwatershed, any flux transported from upstream reaches, and any attenuation (losses) within the reach itself. Nutrient transport from uplands to stream channels and within the stream network was not assumed to be conservative, but rather was weighted by landscape factors affecting overland and in-stream fate and transport (Schwarz and others, 2006; Hoos and McMahon, 2009).

Stream Network Development

The digital network of streams and associated catchments used in SPARROW models for the Chesapeake Bay watershed was developed from the geospatial dataset, NHDPlus, a 1:100,000-scale representation of stream hydrography built upon the National Hydrography Dataset (NHD) (Horizon Systems, 2010; Simley and Carswell, 2010). The development of network and stream characteristics (such as topology and mean annual streamflow) is described in Horizon Systems (2010). Reaches described as lakes, ponds, or reservoirs in NHDPlus were generally modeled as impounded reaches; the outlet reach for each impoundment was identified on the basis of the hydrologic sequence number. All other reaches were modeled as flowing streams. Terminal (target) reaches were generally assumed to be those identified as terminal flowlines in NHDPlus. Modifications to NHDPlus included corrections to stream connectivity and reach types (including flowing, impounded, and (or) terminal reaches) and the addition of stream and watershed attributes particularly relevant to SPARROW modeling (Brakebill and others, 2011). Surface areas of reservoirs on the lower Susquehanna River were compiled from Hainly and others (1995). The fraction of total streamflow delivered by braided reaches or other divergences in the NHDPlus network was compiled from a similar network developed for the wider northeastern United States (Moore and others, 2011). The NHDPlus-based model network used to support SPARROW calibration and predictions for the Chesapeake Bay watershed includes 80,579 reaches assumed to represent nontidal bay tributaries. Also included are an additional 1,329 reaches representing centerlines of tidal reaches of major Chesapeake tributaries; SPARROW predictions for these reaches were used only to estimate the total TN and TP fluxes to the bay.

The NHDPlus digital stream network represents a significant spatial refinement over that used by previous SPARROW models for the Chesapeake Bay watershed. The 80,579 individual nontidal stream reaches in the model area drain local watershed catchments (independent of watersheds of any contributing upstream reaches) with a mean area of 2.1 km^2. Previous SPARROW models for the Chesapeake Bay watershed were constructed on a 1:500,000-scale hydrologic network with 2,734 stream reaches draining catchment areas averaging 75 km^2 in size (Brakebill and others, 2010).

Calibration Data

The SPARROW models were calibrated to independent estimates of mean annual contaminant flux at selected locations on the stream network where water-quality monitoring has been conducted. Annual in-stream TN and TP fluxes on nontidal Chesapeake tributaries used as dependent variables in SPARROW calibration were estimated using multiple regression modeling of available water chemistry and streamflow at monitored sites (Schwarz and others, 2006).

Water-quality data for use in SPARROW calibration were compiled from available surface-water monitoring records collected between 1995 and 2009 by the U.S. Geological Survey (USGS), State agencies, and River Basin Commissions within the Chesapeake Bay watershed. A detailed description of data compilation methods is included in Langland and others (2007). Water-quality records for more than 600 stream sites (water-quality stations) with more than 50 TN and (or) TP observations between October 1970 and December 2009 were compiled and reviewed. In general, only water-quality stations for which a minimum of 5 years of record were available were retained. Stations with unavailable or uncertain location information or for which no water-quality data were available between January 2001 and December 2003 were omitted. In cases where multiple water-quality stations exist within the same local network catchment, only data from the station with the most complete water-quality data were retained. Water-quality observations at two stations within 0.32 km (kilometers) of one another on the Slate River were combined because the periods of record suggest sampling at one station is intended to replace sampling at the other.

Streamflow data collected between 1980 and 2009 were compiled and associated with available water-quality data to support estimates of mean annual TN and TP flux at water-quality stations for use in SPARROW calibration. Streamflow data were compiled from USGS records (U.S. Geological Survey, 2011a) and associated with water-quality data collected at common locations. Water-quality data that were not collected at USGS stream gages were associated to flow data from nearby gages. Of the 205 water-quality stations used for flux estimation, water-quality to flow-station area ratios for 202 were between 0.5 and 1.5; the other three were 0.12 (Chickahominy River), 0.26 (Licking Run), and 1.6 (South Fork, Potomac River).

Water-quality data (observed TN and TP concentrations) and measured or estimated streamflow were used to estimate mean annual TN and TP flux at water-quality stations. Multiple-regression models calibrated to routine chemical observations and continuous streamflow (Cohn and others, 1989; 1992) have been used extensively to estimate contaminant flux in monitored streams (for example, Johnson and Belval, 1998; Langland and others, 2006). For this application, TN and TP flux at water-quality stations in the Chesapeake Bay watershed were estimated using a nine-parameter model including terms for streamflow, time (decimal year), seasonality (sine and cosine of time), and squares of each using the USGS FLUXMASTER statistical routine (G.E. Schwarz, U.S. Geological Survey, written commun., 2008). Where trends in streamflow or water quality were evident, results were detrended to 2002 conditions. Flux estimates were also adjusted to reflect mass flux at the outlet of NHD catchments based on the ratio of the drainage area of the monitoring station to that of the catchment outlet. In cases where streamflow and water-quality measurements were collected on different reaches, flux estimates were similarly adjusted based on the ratio of the streamflow station area to NHD catchment area for the water-quality station. Diagnostics (including standard errors and residual distributions) were reviewed for each flux model, and TN or TP estimates from nine-parameter models that were considered unreliable were discarded and replaced with those from a simpler seven-parameter model lacking squared time and streamflow terms. Residual analysis suggested that the squared streamflow term can contribute substantial error in such flux models, particularly where data are sparse.

Flux estimates from across the Chesapeake Bay watershed were normalized and are therefore not subject to regional variations in hydrologic (for example, flood or drought) conditions. Mean annual TN and TP fluxes for use in SPARROW calibration were estimated using water-quality data available for a 15-year period centered on 2002 (1994 through 2009) and were adjusted (where possible) to reflect mean hydrologic conditions estimated from a 30-year flow record. Flux estimates for use in SPARROW calibration thus represent long-term mean conditions and generally eliminate potential effects of spatially variable hydrologic conditions within the watershed during the target year (2002). Available long-term flow data were used to calculate TN and TP flux estimates that represent the flux that would have occurred at each site during 2002 had long-term mean hydrologic conditions occurred.

Available calibration data for the SPARROW models reflect the spatial and temporal distributions of streamflow and surface-water-quality monitoring in the Chesapeake Bay watershed. The SPARROW models were calibrated to mean annual TN and TP flux estimates for 2002 at 181 and 184 water-quality stations, respectively (fig. 3). In general, streamflow and water-quality monitoring (and therefore available TN and TP flux estimates for SPARROW calibration) are located disproportionately on larger Chesapeake tributaries, and lower-order streams are poorly represented (fig. 4). The 80,579 nontidal stream reaches in the SPARROW network drain watersheds with a median total area of 5.0 km^2; the smallest stream for which TN and TP flux estimates could be computed, however, drains a watershed more than twice that size (12.6 km^2). SPARROW models calibrated with available flux estimates might be expected to reasonably represent TN and TP fluxes in larger Chesapeake tributaries, but improved understanding of TN and TP flux and processes in smaller watersheds might require more water-quality and streamflow data collected in particularly small streams.

Explanatory Data

Explanatory variables developed for use in SPARROW model calibration include spatially explicit and spatially comprehensive nutrient sources and watershed characteristics representative of processes significant to nutrient fate and transport (Schwarz and others, 2006). Explanatory variables representing TN and TP sources and transport factors were apportioned to stream reaches and associated watershed catchments and serve as independent variables in SPARROW calibration.

Many of the explanatory variables considered for the model were extracted from those developed from geospatial data for similar models of large watersheds in the United States as part of the National Water-Quality Assessment (NAWQA) Program (Preston and others, 2011). Briefly, an inverse-distance weighting approach was used to interpolate data from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (U.S. Geological Survey, 2000; Alexander and others, 2001) to estimate wet atmospheric inorganic nitrogen deposition to model watersheds in 2002 (Wieczorek and LaMotte, 2010a). Available land-cover data for 2001 (Wieczorek and LaMotte, 2010b) and estimated inputs of nitrogen and phosphorus in fertilizer, fixation by crops, and manure in 2002 (Wieczorek and LaMotte, 2010c, d) were compiled and similarly apportioned to catchments within the model network, along with soil conditions and other watershed characteristics potentially relevant to nitrogen or phosphorus fluxes (Wieczorek and LaMotte, 2010e, f, g, h). Estimates of annual nitrogen and phosphorus discharges from (primarily municipal) point sources during 2002 to Chesapeake tributaries were compiled by the Chesapeake Bay Program (U.S. Environmental Protection Agency, 2009). Physiography and geology in the Chesapeake Bay watershed were compiled from Bachman and others (1998) and Brakebill and Kelley (2000). The enhanced vegetative index (EVI) for 2002, a globally consistent measure of vegetation conditions, was interpreted from data compiled from the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument onboard the Earth Observing System-Terra platform at 1-km resolution and 16-day compositing periods (Huete and others, 2002).

SPARROW Model Calibration and Predictions

SPARROW models of TN and TP for the Chesapeake Bay watershed (CBTN_v4 and CBTP_v4) were calibrated from compiled data. A detailed discussion of the nonlinear regression and bootstrapping approach used to calibrate SPARROW models, estimate model coefficients, and predict contaminant flux in unmonitored streams is available in Schwarz and others (2006). Individual explanatory variables for potential inclusion in each Chesapeake SPARROW model were selected on the basis of current understanding of nutrient occurrence, fate, and transport in the watershed available through previous studies, including previous models for the Chesapeake Bay watershed (Preston and Brakebill, 1999; Brakebill and others, 2001; Brakebill and Preston, 2004) and the wider northeastern United States (Moore and others, 2011). Models were generally constructed by including source terms, land-to-water variables, and aquatic (flowing and impounded) decay specification, in turn (Schwarz and others, 2006). Nutrient source and aquatic decay variables were constrained to be non-negative in model calibration; land-to-water variables were not constrained. Nonlinear least-squares regression was used to calibrate exploratory models during model development; bootstrapping (which uses random resampling to infer the distribution of parameter estimators, Schwarz and others, 2006) was used to verify coefficient estimates in the final models and to estimate confidence intervals for predictions. Many different combinations of explanatory variables were included in preliminary model development. The final list of explanatory variables and the form of each model were determined through consideration of the overall model explanatory power and the geographic and statistical distribution of residuals, as well as the significance of each variable, its collinearity with other variables, and its contribution to the understanding of nutrient occurrence, fate, and transport.

Explanatory variable specifications in the SPARROW models were chosen to maximize the interpretability of model coefficients and comparability with literature values, as well as to support estimation of TN and TP fluxes in unmonitored areas (Schwarz and others, 2006). Source terms in the models are specified as either the estimated mass of nitrogen or phosphorus applied or deposited annually to each local catchment, or the area of a specific land cover or geologic setting.

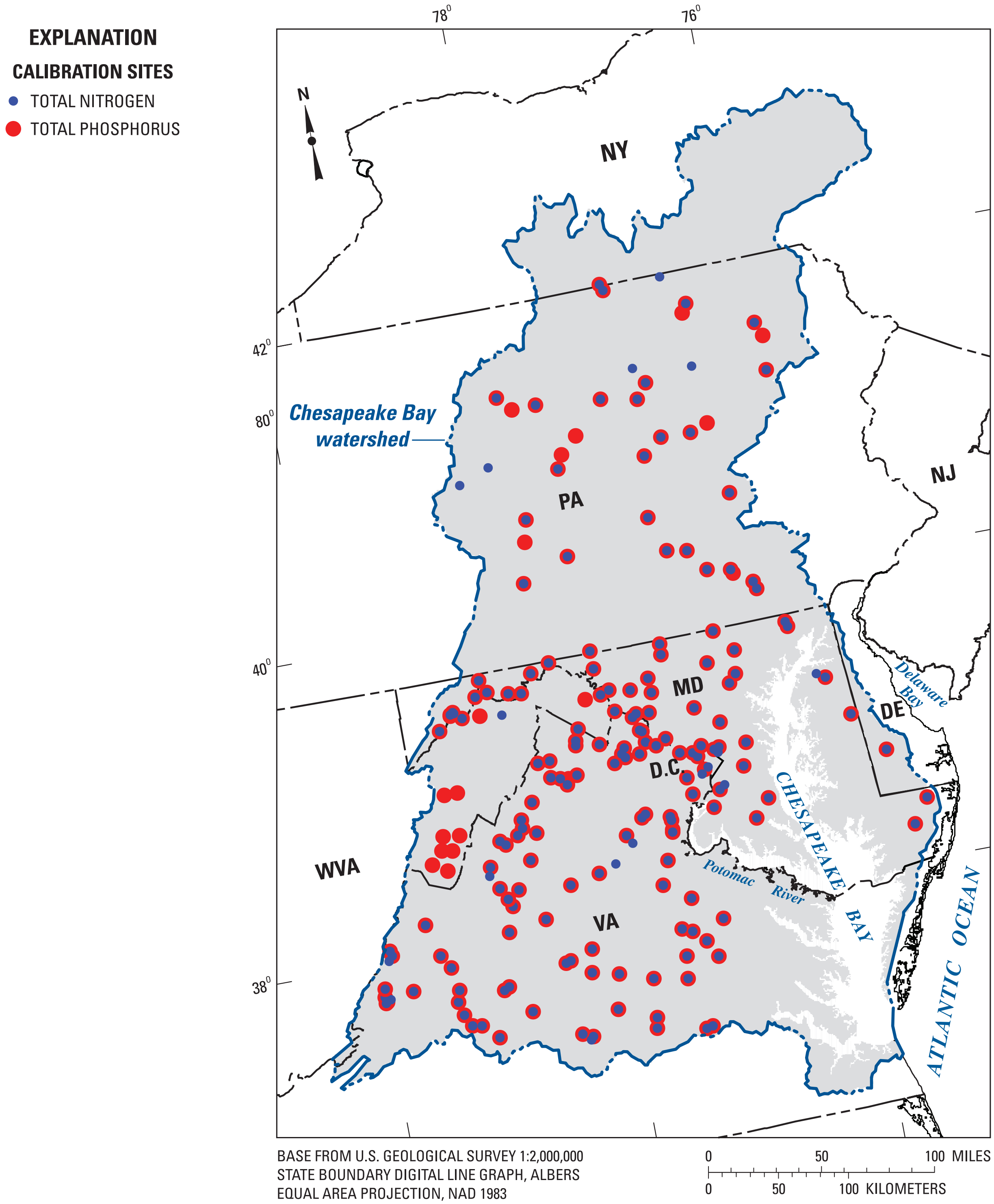

Figure 3. Location of stations for which mean annual flux estimates of total nitrogen and (or) total phosphorus were computed for use in SPARROW model calibration.

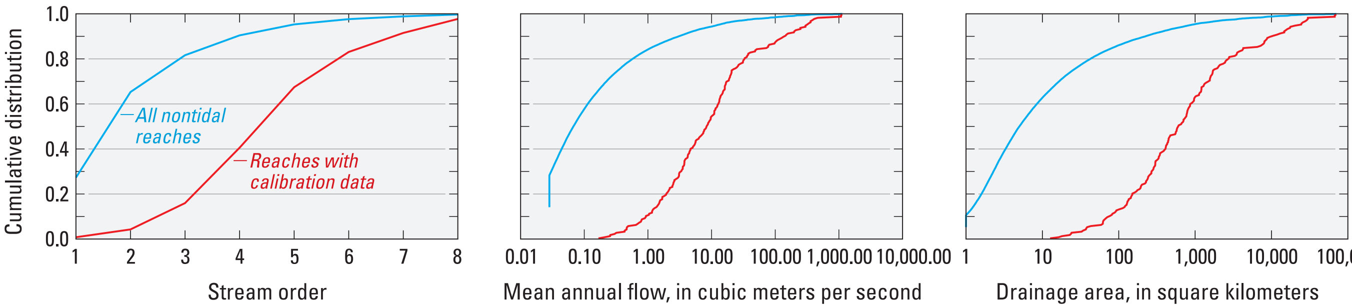

Figure 4. The distribution of stream order, streamflow, and watershed size among modeled stream reaches in the Chesapeake Bay watershed, and those with calibration stations.

Estimated coefficients are thus interpreted as the proportion (fraction) of the applied or deposited nutrient mass transported to watershed streams, or the mean yield of TN or TP from the land cover or geologic setting, respectively. Generally, explanatory terms affecting nutrient transport from the land to streams (land-to-water terms) were specified in the models to interact with (potentially increase or decrease delivery of TN or TP to streams from) all sources except for point sources; terrestrial processes were assumed to be irrelevant for point sources discharging directly to streams. Soil erodibility (K-factor) in the TP model does not interact with the crystalline or siliciclastic rock sources, which are intended to represent natural sources of phosphorus to groundwater (Denver and others, 2010). The Coastal Plain term in the TP model similarly does not interact with these rock sources; there are no crystalline or siliciclastic rocks near the land surface in the Coastal Plain (Ator and others, 2005). Land-to-water terms were centered (mean-adjusted) and generally log-transformed; coefficients for log-transformed terms can be interpreted as the percent change in flux delivered to streams from each interacting source term for a 1-percent increase in each land-to-water variable (Schwarz and others, 2006). Instream nutrient losses (decay) in flowing streams were modeled as a first-order decay process and specified as a function of estimated time of travel (based on the stream reach length and estimated velocity, Horizon Systems, 2010), and coefficients can be interpreted as the mean annual rate of TN or TP removal within the stream reach. Decreasing rates of in-stream nitrogen decay with increasing stream size have been observed in previous SPARROW models in the Chesapeake Bay watershed (Preston and Brakebill, 1999) and elsewhere (Smith and others, 1997); denitrification and biotic nutrient uptake occur primarily in the benthic zone, and smaller streams typically support less streamflow per benthic area (Schwarz and others, 2006). Also, biological processes controlling nutrient uptake may increase with increasing temperature (Bothwell, 1988) and preliminary TN SPARROW models suggested a corresponding trend in TN residuals. In-stream losses were therefore modeled separately for classes of stream reaches defined by estimated mean annual flow (Horizon Systems, 2010) and mean annual maximum surface-air temperature from 1971 through 2000 (fig. 5); flow and temperature values defining different classes were selected based on results of preliminary models using various multiple arbitrary values (Preston and Brakebill, 1999). Losses in impoundments (lakes, ponds, and reservoirs) are specified as the inverse of the areal hydraulic load (the ratio of reservoir outflow to surface area) and estimated coefficients can be interpreted as an apparent settling velocity (Schwarz and others, 2006). In general, only terms significantly different from zero (α=0.10) were retained in the models. One term representing stream decay (aquatic decay in flowing streams) with a higher p-value was retained in the TN model, however; the estimated decay in this class of streams was more than ten times smaller than in other classes, as expected in light of mean annual flow (Preston and Brakebill, 1999) and air temperature (Bothwell, 1988). For the purpose of calibration, missing values for source or decay variables were assumed to be zero; missing values for land-to-water terms were set to the median of non-missing values.

SPARROW models were used to predict the spatial distribution of TN and TP fluxes within Chesapeake tributaries and the total flux of TN and TP to the bay (Schwarz and others, 2006). Estimated model coefficients were used along with values of explanatory terms in each catchment to estimate the total and local flux of TN and TP (overall, and from each source) for each stream in the model network (see Appendix). Predicted TN and TP fluxes at monitoring reaches (those with calibration data) were adjusted to match calibration data. Total TN and TP flux from the watershed to Chesapeake Bay was estimated as the sum of total estimated TN and TP flux at downstream terminal reaches in the model network.

Although SPARROW is not designed for modeling tidal waters, 1,329 reaches representing centerlines of tidal parts of major Chesapeake tributaries are included in the

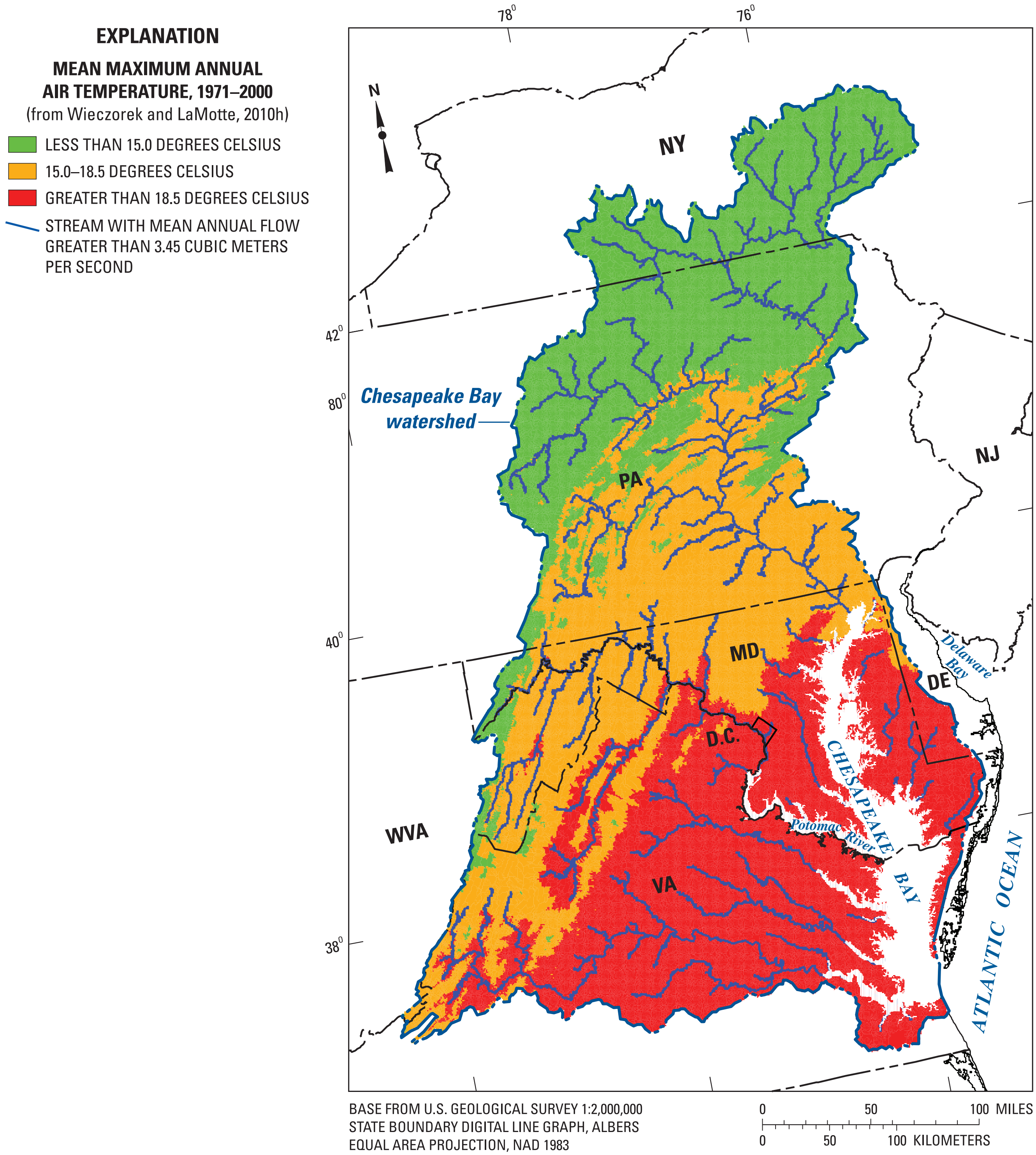

Figure 5. Mean annual maximum air temperature, 1971–2000, and streams with mean annual flow greater than 3.45 cubic meters per second.

NHDPlus-based model network along with the 80,579 nontidal tributary reaches, and TN and TP flux predictions were therefore also estimated for these reaches. Although predictions for these 1,329 centerline reaches are generally not presented in this report (on, for example, maps of TN or TP yields), they were included in estimating total TN and TP fluxes to Chesapeake Bay, which therefore include nutrient inputs (such as from point sources and atmospheric deposition) directly to major tidal tributaries. Predictions for these reaches also are included in the accompanying datafile for that purpose (see Appendix), although these predictions for tidal waters are not intended for other uses. Stream decay was not applied to centerline reaches for the purpose of these estimates; stream decay is calibrated in the SPARROW models to flowing reaches and is not intended to represent nutrient decay in tidal waters. Estimates of total TN and TP fluxes to Chesapeake Bay can therefore be interpreted to include all modeled terrestrial and atmospheric sources to tidal and nontidal tributaries and the effects of overland and fluvial transport, but not effects of losses or other processes in tidal waters.

Model Limitations

Predictions from the CBTN_v4 and CBTP_v4 SPARROW models for the Chesapeake Bay, like those of all models, must be considered in light of the assumptions and simplifications inherent in the model specification and the limitations of available input data. Assumptions and simplifications inherent to SPARROW are discussed in Schwarz and others (2006). The models do not include all possible nutrient sources; minor sources or those for which spatially explicit estimates are not available may be incorporated by SPARROW into other source terms and (or) contribute to model uncertainty. The models reflect mean annual conditions over long periods, and the effects of processes or activities over seasons or other relatively short time periods are not represented. Estimation of TN and TP fluxes for use in SPARROW calibration and the development and allocation of much of the explanatory data were done with other statistical or geographic models that are limited by their own assumptions and simplifications. Water-quality data in the Chesapeake Bay watershed suitable for SPARROW calibration may be very representative of conditions in relatively large streams, but smaller streams are poorly represented. Headwater streams are typically most closely linked to adjacent uplands and associated contaminant sources, drain the majority of larger watersheds, and contribute directly to streams of all sizes (Alexander and others, 2007). Nearly half (45 percent) of the nitrogen delivered to streams in the northeastern United States is delivered to headwater streams (Alexander and others, 2007).The increasing availability of stream hydrography at finer resolution (for example 1:100,000 scale for the current models) underscores the potential usefulness of increased water-quality and streamflow monitoring on small streams to support a better understanding of nutrient dynamics in those systems within regional models.

Nitrogen and Phosphorus in the Chesapeake Bay Watershed

The calibrated CBTN_v4 and CBTP_v4 SPARROW models identify and quantify significant sources of nitrogen and phosphorus, landscape characteristics affecting the delivery of nutrients to streams, losses within flowing and impounded streams, and estimated local (generated within each individual catchment) and delivered (to downstream estuaries) fluxes and yields for each of 80,579 streams in the Chesapeake Bay watershed. Explanatory terms in the TN model explain 98 percent of the spatial variability in mean annual TN flux estimates at the 181 calibration sites and 86 percent of the variability in TN yields (table 1). Explanatory terms in the TP model similarly explain a significant part of the variability in the TP calibration data; flux-R^2 and yield-R^2 values for the TP model are 0.951 and 0.730, respectively (table 2). Relatively high flux-R^2 values in SPARROW models are due in part to the natural correlation between watershed area and contaminant flux, and yield-R^2 values are therefore likely more indicative of the explanatory value of model terms (Schwarz and others, 2006).

Watershed Sources

A variety of natural and human sources contribute nitrogen and phosphorus to the Chesapeake Bay watershed. Anthropogenic sources of nutrients that are significant (greater than zero, α=0.10) in the TN and TP SPARROW models include point sources, certain urban activities, and fertilizer and manure applications in agricultural areas (tables 1, 2). Significant sources of nitrogen also include direct fixation of atmospheric nitrogen by certain crops, and deposition from the atmosphere. Natural mineral sources in siliciclastic and crystalline rocks contribute significantly to the phosphorus flux in streams.

Point sources input nutrients directly to streams in the Chesapeake Bay watershed (fig. 1; tables 1, 2). Point sources contribute both TN and TP to Chesapeake tributaries; the point source coefficient is near one in each model, as would be expected given that point sources discharge directly to streams with no opportunity for terrestrial losses. Most streams in the watershed receive no direct nitrogen or phosphorus inputs from point sources. Point sources can contribute substantially (more than 99 percent) to local TN or TP fluxes where they occur, however, and produce extremely high local yields.

Agriculture contributes significantly to nonpoint nitrogen and phosphorus inputs in the Chesapeake Bay watershed. Approximately 24 percent of estimated nitrogen applications in fertilizers and direct fixation by crops reaches watershed streams (table 1). Howarth and others (1996) estimated that 25 percent of nonpoint nitrogen applications (including from fertilizers and fixation by leguminous crops) from temperate regions is transported to streams draining to the North Atlantic

Table 1. Summary of nonlinear least-squares calibration results for CBTN_v4, the Chesapeake Bay watershed total nitrogen model.

[MSE, mean squared error; RMSE, root mean squared error; kg, kilogram; yr, year; km^2, square kilometer; EVI, enhanced vegetative index; AWC, available water capacity; m, meter; mm, millimeter; d, days; WY02, water year 2002 (October 2001 through September 2002); MAQ, mean annual flow; $m^3 s^{-1}$, cubic meters per second; T30, mean annual maximum temperature from 1971 through 2000; °C, degrees Celsius; <, less than; >, greater than; ≤, less than or equal to]

Total Nitrogen, 2002 (n = 181, MSE = 0.0836, RMSE = 0.289, flux R^2 = 0.978, yield R^2 = 0.858)					
Explanatory variables	**Estimate**	**Units**	**90-percent confidence interval**	**Standard error**	**p[1]**
Sources					
Point sources (kg yr^{-1})	0.774		0.375 – 1.17	0.242	0.0008
Crop fertilizer and fixation (kg yr^{-1})	0.237		0.177 – 0.297	0.0363	< 0.0001
Manure (kg yr^{-1})	0.0582		0.0138 – 0.103	0.0269	0.0157
Atmospheric deposition (kg yr^{-1})	0.267		0.179 – 0.355	0.0533	< 0.0001
Urban[2] (km^2)	1,090	kg km^{-2} yr^{-1}	707 – 1,480	234	< 0.0001
Land-to-water delivery					
ln[Mean EVI for WY02 (dimensionless)]	-1.70		-2.65 – -0.737	0.580	0.0039
ln[Mean soil AWC (fraction)]	-0.829		-1.26 – -0.401	0.260	0.0016
ln[Groundwater recharge (mm)]	0.707	mm^{-1}	0.499 – 0.916	0.126	< 0.0001
ln[Piedmont carbonate (percent of area)]	0.158		0.0755 – 0.241	0.0500	0.0018
Aquatic decay					
Impoundments, inverse hydraulic load (yr m^{-1})	5.93	m yr^{-1}	0.271 – 11.6	3.42	0.0424
Streams, time of travel (d) in:					
Small (MAQ ≤ 3.45 $m^3 s^{-1}$)	0.339	d^{-1}	0.0936 – 0.585	0.148	0.0118
Large (MAQ > 3.45 $m^3 s^{-1}$), T30 > 18.5°C	0.153	d^{-1}	0.0622 – 0.245	0.0551	0.0030
Large (MAQ > 3.45 $m^3 s^{-1}$), T30 ≤ 15°C	0.0131	d^{-1}	-0.111 – 0.137	0.0751	0.431

[1] p-values are one-sided for sources and aquatic-decay coefficients (which were constrained to be non-negative) and two-sided for land-to-water delivery coefficients.

[2] Urban land includes all developed land, as defined by Wieczorek and LaMotte, 2010b.

Ocean, and Preston and Brakebill (1999) estimated that 28 percent of nitrogen from fertilizer applications was transported to Chesapeake tributaries in 1987. Conversely, less than 6 percent of TN from manure and TP from both fertilizers and manure is transported to watershed streams (tables 1, 2). Organic nitrogen in manure and phosphorus compounds generally are less soluble and therefore, mobile in the environment than inorganic nitrogen compounds commonly applied as fertilizers (Hem, 1985). Also, nitrogen and phosphorus in animal wastes may be largely recycled from other local sources (such as locally grown feed), and relatively little nitrogen or phosphorus in manure may represent a net influx of nutrients to local watersheds such as that in chemical fertilizers and fixation from the atmosphere (Howarth and others, 1996). Moore and others (2011) similarly reported substantially lower export coefficients for TN and TP from manure than from fertilizers for a wider area of the northeastern United States, although Preston and Brakebill (1999) reported similar export coefficients for TN from fertilizers and manure in the Chesapeake Bay watershed in 1987.

Unlike point sources, agriculture is widespread within the Chesapeake Bay watershed, and fertilizer and manure applications represent significant sources of TN and TP to streams in many areas. Agriculture in the Chesapeake Bay watershed occurs primarily in the northern Piedmont, the Eastern Shore of the Coastal Plain (the Delmarva Peninsula), and in isolated valleys in the mountainous areas, particularly the Great Valley from Virginia through Pennsylvania (figs. 1, 2). Predicted local yields of TN and TP from agricultural sources (fertilizers, manure, and crop fixation) are accordingly highest in these areas (fig. 6). Local yields of nutrients from manure are particularly high in the southern Shenandoah Valley, the lower

Table 2. Summary of nonlinear least-squares calibration results for CBTP_v4, the Chesapeake Bay watershed total phosphorus model.

[MSE, mean squared error; RMSE, root mean squared error; kg, kilogram; yr, year; km^2, square kilometer; mm, millimeter; m, meter; <, less than]

Total Phosphorus, 2002 (n = 184, MSE = 0.225, RMSE = 0.474, flux R^2 = 0.951, yield R^2 = 0.730)					
Explanatory variables	**Estimate**	**Units**	**90-percent confidence Interval**	**Standard error**	**p[1]**
Sources					
Point sources (kg yr^{-1})	0.877		0.573 – 1.18	0.183	< 0.0001
Crop fertilizer (kg yr^{-1})	0.0377		0.0171 – 0.0583	0.0125	0.0014
Manure (kg yr^{-1})	0.0253		0.0144 – 0.0362	0.00658	0.0002
Siliciclastic rocks (km^2)	8.52	kg km^{-2} yr^{-1}	6.10 – 10.9	1.46	< 0.0001
Crystalline rocks (km^2)	6.75	kg km^{-2} yr^{-1}	3.25 – 10.2	2.12	0.0009
Urban[2] (km^2)	49.0	kg km^{-2} yr^{-1}	30.4 – 67.7	11.3	< 0.0001
Land-to-water delivery					
Soil erodibility (K factor)	6.25		3.55 – 8.95	1.63	0.0002
ln[Well-drained soils (percent)]	-0.100		-0.153 – -0.0478	0.0317	0.0019
Coastal Plain (percent of area)	1.02		0.681 – 1.35	0.204	< 0.0001
ln[Precipitation[3] (mm)]	2.06	mm^{-1}	0.567 – 3.55	0.903	0.0237
Aquatic decay					
Impoundments, inverse hydraulic load (yr m^{-1})	54.3	m yr^{-1}	12.1 – 96.5	25.5	0.0174

[1] p-values are one-sided for sources and aquatic-decay coefficients (which were constrained to be non-negative) and two-sided for land-to-water delivery coefficients.

[2] Urban land includes all developed land, as defined by Wieczorek and LaMotte, 2010b.

[3] Mean annual precipitation, 1971 through 2000.

Delmarva Peninsula, and southeastern Pennsylvania, where livestock (primarily poultry and cattle) production is greatest, and manure represents the majority of local TP sources and nearly half of local TN sources to these areas. Local yields from fertilizer applications and crop fixation are more evenly distributed throughout agricultural areas of the watershed, and represent the majority of local TN and TP yields from all sources in many areas.

Urban areas yield, on average, 1,090 kg km^{-2} yr^{-1} (kilograms per square kilometer per year) of TN and 49 kg km^{-2} yr^{-1} of TP to streams in the Chesapeake Bay watershed. Individual urban sources of TN and TP are generalized and not distinguished by the SPARROW models, but may include fertilizer applications to turf grasses, septic systems, leaking sewer lines, domestic animals, local deposition from automobiles, or spills in commercial or industrial areas. Like point sources, urban areas are limited spatially within the watershed, but may contribute substantially to in-stream TN and TP fluxes in isolated urban areas.

Atmospheric deposition contributes significantly to TN export in streams throughout the Chesapeake Bay watershed. Although nitrogen gas is naturally abundant in the atmosphere, atmospheric wet deposition of inorganic nitrogen is derived primarily from emissions generated by the combustion of fossil fuels and from certain agricultural activities (Driscoll and others, 2003). An estimated 27 percent of atmospheric nitrogen deposition reaches streams of the watershed (table 1), which is similar to previous estimates for nonpoint nitrogen applications from temperate areas draining to the North Atlantic Ocean (Howarth and others, 1996) and for streams of the northeastern United States (Moore and others, 2011). Unlike other sources, atmospheric deposition occurs within

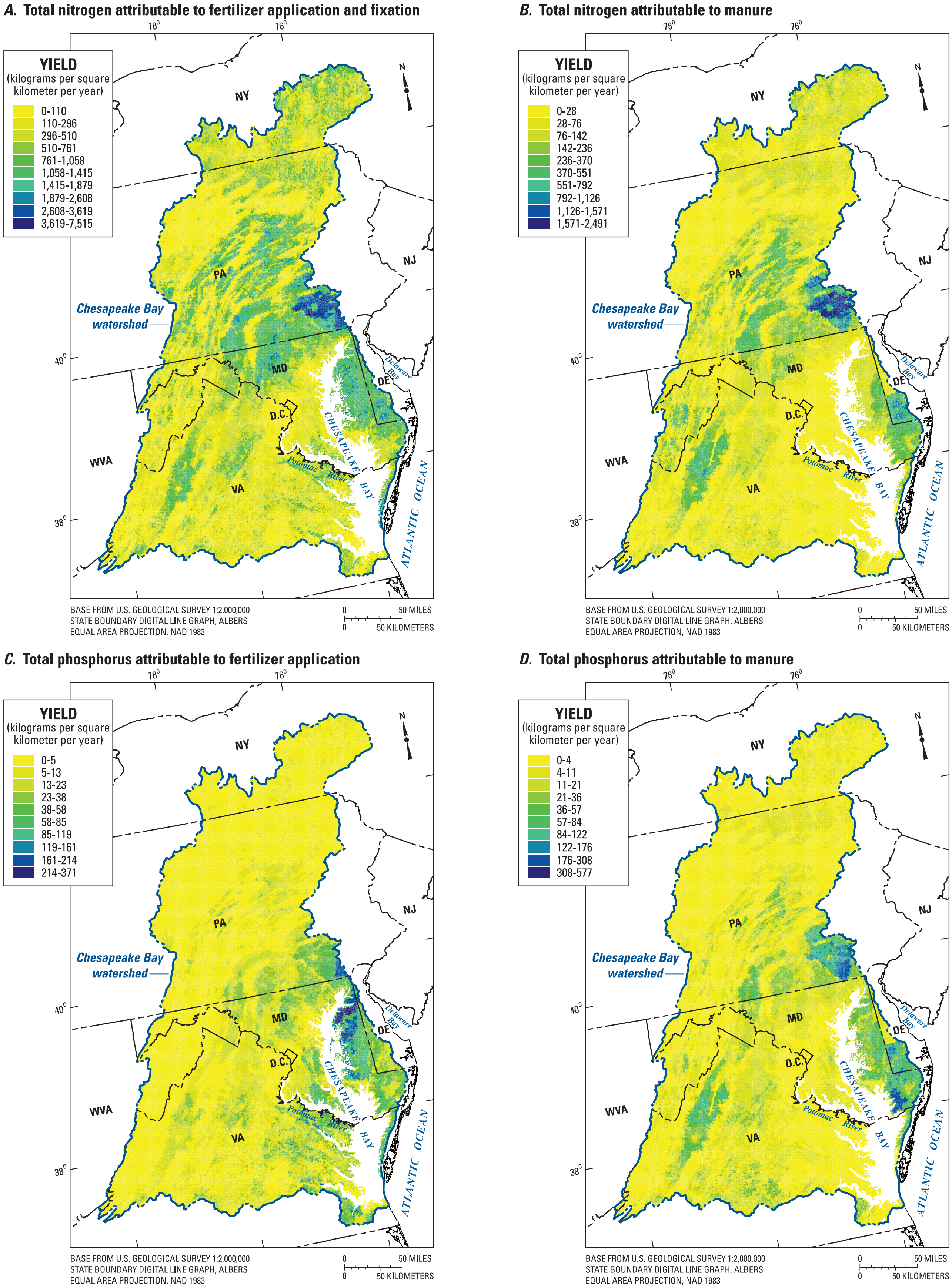

Figure 6. Estimated local yields of total nitrogen and phosphorus from agricultural sources.

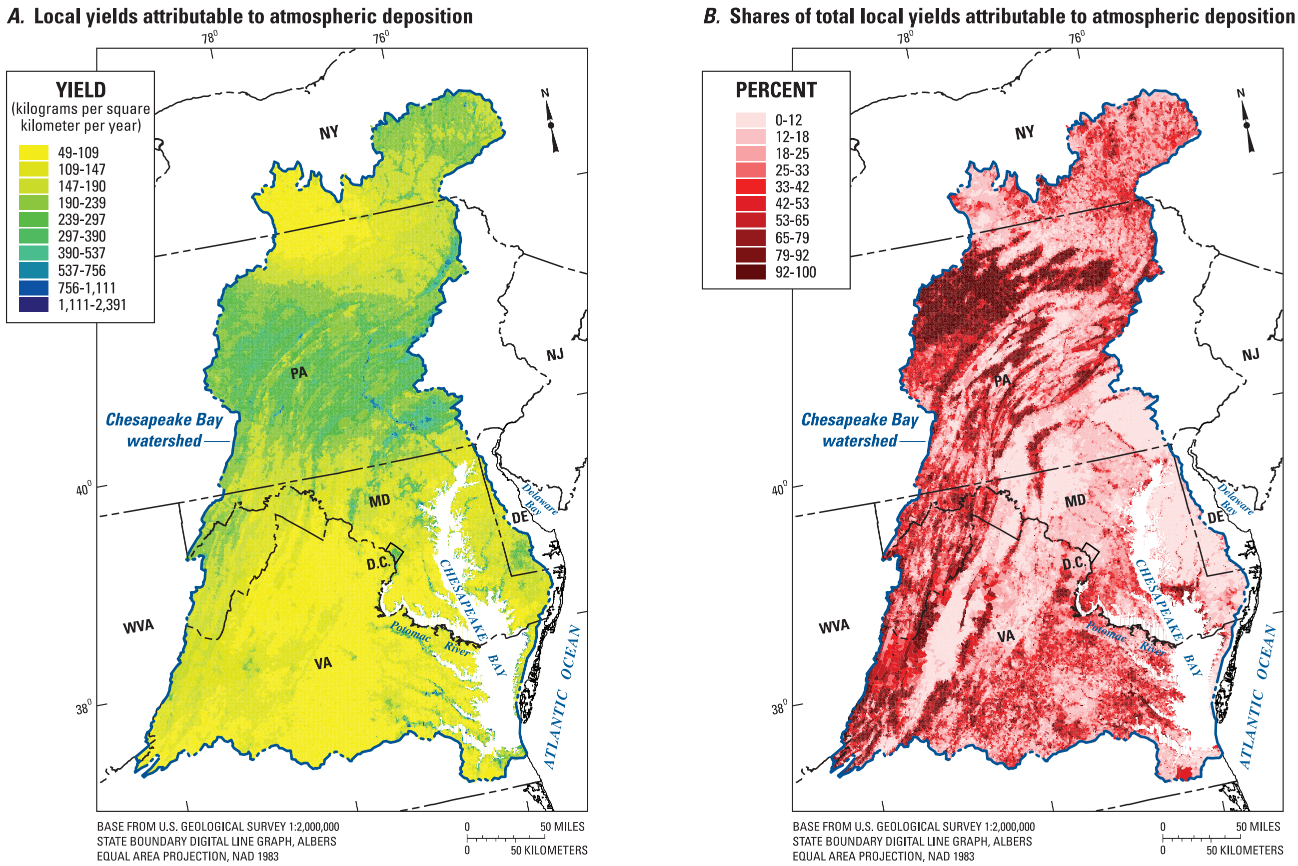

Figure 7. Estimated local *(A)* yields and *(B)* source shares of total nitrogen from atmospheric deposition.

each individual catchment within the Chesapeake Bay watershed (fig. 7a), and represents the majority of TN sources in northern and western forested areas (particularly in western Pennsylvania and Virginia), where other nitrogen sources are limited (fig. 7b).

Minerals in crystalline and siliciclastic rocks represent natural sources of TP export in some areas of the Chesapeake Bay watershed. Forested areas have been noted as significant TP sources in previous SPARROW models (for example, Alexander and others, 2008; Moore and others, 2011), and likely represent a proxy for any background phosphorus sources not accounted for by other source terms. Crystalline and siliciclastic rocks in the eastern Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces have been identified as likely sources of dissolved phosphorus to groundwater and—by extension—to receiving streams (Denver and others, 2010), however, and may be the source of TP exports noted from forested areas in previous models. The estimated mean yields of 6.8 and 8.5 kg km^{-2} yr^{-1} of phosphorus from areas of the Chesapeake Bay watershed underlain by crystalline and siliciclastic rocks (respectively) (table 2) are similar to mean exports reported by Dillon and Kirchner (1975) for natural forested areas underlain by similar rocks in southern Ontario (4.8 kg km^{-2} yr^{-1} and 10.7 kg km^{-2} yr^{-1} for granitic igneous and sedimentary rocks, respectively), and to phosphorus exports from natural forested watersheds in other temperate areas (Dillon and Kirchner, 1975; Likens and others, 1977). Phosphorus yields from mineral sources are generally much smaller than from other sources where they exist, but represent the majority of the small TP flux from relatively natural areas, particularly in the northern and western mountainous areas of the Chesapeake Bay watershed (fig. 8).

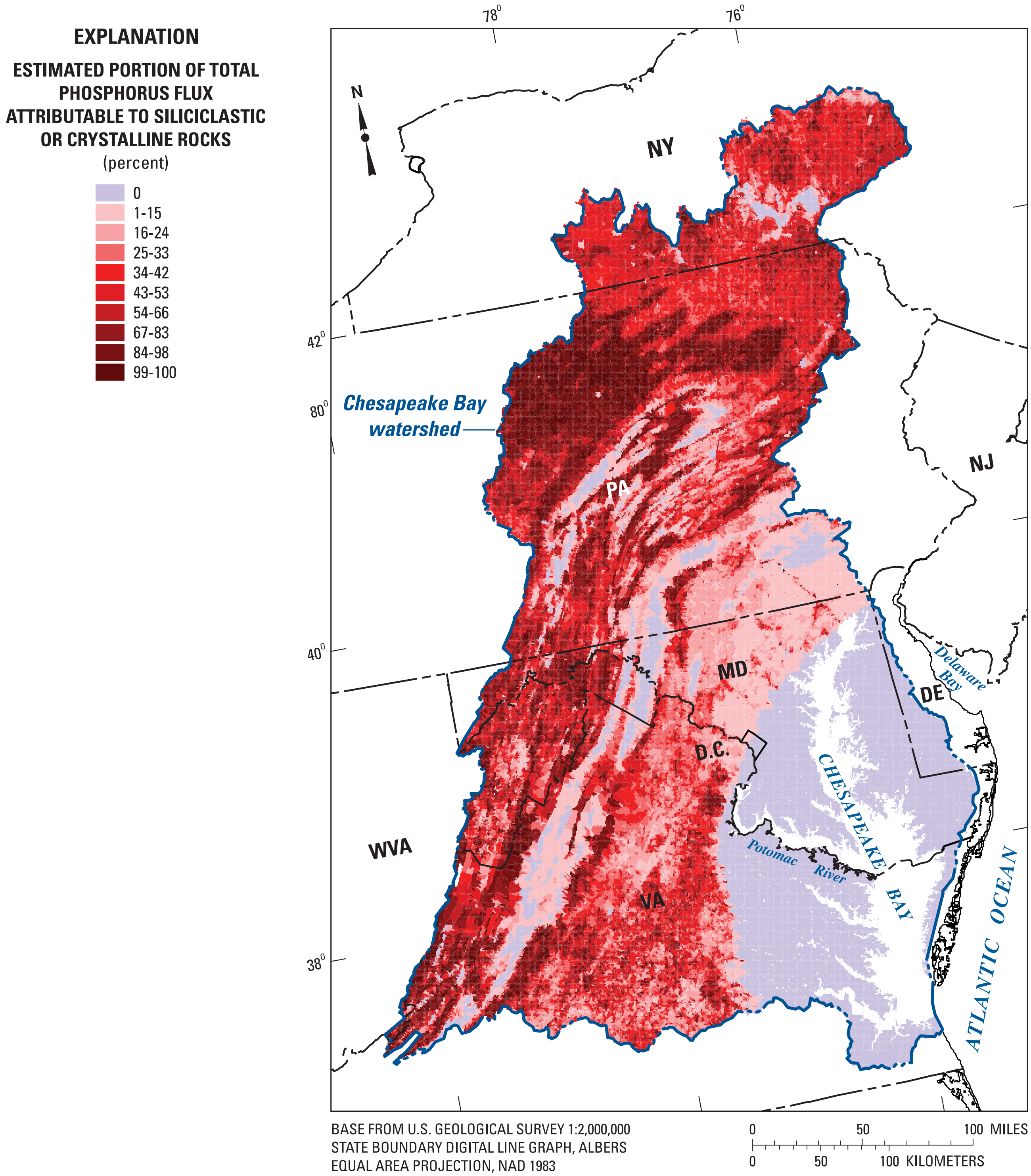

Figure 8. Share of local phosphorus yields attributable to siliciclastic or crystalline rocks.

Fate and Transport

Nitrogen and phosphorus are typically not transported conservatively through the environment, but are subject to a variety of mostly biologically mediated losses and transformations in both terrestrial and aquatic settings. Fate and transport processes relevant to nitrogen and phosphorus are represented in the SPARROW models by land-to-water and aquatic decay terms selected to represent known factors contributing to the spatial distribution of these nutrients in groundwater and streams of the watershed. Land-to-water terms selected for the TN model reflect major factors controlling the fate, transport, and (therefore) occurrence of nitrogen in the Chesapeake Bay watershed and vicinity, including plant uptake, redox conditions, and hydrogeologic conditions important to nitrate transport through groundwater. Conversely, phosphorus compounds are relatively insoluble, and land-to-water terms in the TP model generally reflect the importance of transport through overland runoff.

Land-to-water terms in the TN model reflect the importance of plant uptake, redox conditions, and groundwater to the fate and transport of nitrogen in the Chesapeake Bay watershed. Decreasing TN delivery to streams in areas of greater EVI (greener) (table 1) likely reflects healthier plant growth and the incorporation of nitrogen in plant biomass rather than groundwater or streams. TN delivery to streams increases with increasing groundwater recharge and is greater in areas underlain by carbonate rocks in the Piedmont than in other areas (table 1). Assuming no net change in aquifer storage (and neglecting withdrawals), areas with greater groundwater recharge will similarly yield greater groundwater discharge to streams. Nitrate in groundwater discharge contributes nearly half of nitrogen flux to streams in the Chesapeake Bay watershed (Phillips and others, 1999), and significantly greater nitrate concentrations in groundwater and concentrations and yields in streams in areas underlain by carbonate bedrock than in areas underlain by other rock types are well documented (for example, Ator and Denis, 1997; Lizarraga, 1997; Miller and others, 1997; Ator and Ferrari, 1998; Greene and others, 2005). The importance of carbonate rocks to nitrogen transport is apparent in particularly high predicted yields of TN from fertilizers in parts of the northern Piedmont (fig. 6a). The existence of carbonate rocks in the Valley and Ridge or Appalachian Plateau (or overall in the watershed) do not constitute significant positive land-to-water terms in the TN model, perhaps due to different types or intensity of sources than in areas of the Piedmont carbonate. Although the Piedmont carbonate area is predominantly agricultural, for example, areas of the Appalachian Plateau and Valley and Ridge underlain by carbonate rocks support more of a mixture of land uses (Phillips and others, 1999). Nitrogen losses through denitrification are common in reducing (generally anoxic or suboxic) waters of the Chesapeake Bay watershed (Miller and others, 1997; Ator, 2008; Denver and others, 2010), and soil denitrification causes the single greatest nitrogen losses in the Susquehanna, Potomac, James, and Rappahannock watersheds (Van Breemen and others, 2002). The importance of redox conditions to TN flux is represented in the SPARROW model by available water capacity (AWC) of soils (table 1). AWC is generally greater in soils with greater organic matter and finer texture (U.S. Department of Agriculture, 1998), and increasing AWC may be indicative of relatively poorly drained reducing areas.

Phosphorus compounds are generally much less soluble than nitrate, and phosphorus delivery from the land surface to streams generally occurs predominantly in suspended form, often attached to sediment (Hem, 1985). Land-to-water terms in the phosphorus model therefore generally represent the likelihood of overland runoff and soil erosion; TP delivery is greater in areas with greater average precipitation and where soils are more erodible and less well-drained and therefore more likely to promote runoff rather than infiltration of precipitation (table 2). The significance of the Coastal Plain as a land-to-water term may reflect increasing phosphorus saturation of soils in that area and resulting decreasing soil retention of applied phosphorus compounds. Phosphorus inputs to cropland on the Delmarva Peninsula are approximately double that removed at harvest, and phosphorus has consequently accumulated in soils at an average annual rate of approximately 10 to 15 kg ha^{-1} (kilograms per hectare) (Staver and Brinsfield, 2001).

Impoundments significantly decrease in-stream fluxes of both TN and TP (tables 1, 2). The estimated mean settlement velocity of 5.9 m yr^{-1} (meters per year) in the TN model (table 1) suggests that denitrification is the main cause of nitrogen loss in watershed impoundments; algal uptake is typically more efficient and has been observed at higher rates, generally greater than 25 m yr^{-1} (Alexander and others, 2002; Schwarz and others, 2006). The mean loss rate of TP in impoundments is considerably higher (54.3 m yr^{-1}, table 2) than that of TN, as might be expected if settling of particulates is the main cause for lost TP from the water column. Mean settlement rates for suspended sediment in reservoirs are generally much higher than those of TN or TP (Schwarz and others, 2006; Brakebill and others, 2010). The implications of these estimated coefficients may be important for future management of the Chesapeake Bay watershed, as the TN estimate suggests most of the nitrogen is lost permanently to the atmosphere, whereas most of the TP is merely stored in impoundments and may be remobilized in the future.

Significant nitrogen losses occur within flowing streams as well as impoundments in the Chesapeake Bay watershed. Although aquatic decay in flowing streams was not significant in the TP model (table 2), significant decay terms were included in the TN model (table 1). Mean estimated decay is greatest in the smallest 90 percent of streams [with mean annual flow less than 3.45 m^3 s^{-1}(cubic meters per second) (122 cubic feet per second)] in the Chesapeake Bay watershed (table 1), and the mean estimate of 0.34 m yr^{-1} is consistent with previous estimates for similar streams (Preston and Brakebill, 1999; Schwarz and others, 2006). The mean estimated rate of TN decay in larger streams (with mean annual flow greater than or equal to 3.45 $m^3 s^{-1}$) is more than an order of magnitude greater where the mean-maximum air temperature is greater than 18.5°C (degrees Celsius) than in cooler areas less than or equal to 15°C (table 1). A similar geographic pattern in nitrogen fate and transport has been observed previously; Boyer and others (2002) estimated that the Susquehanna and Potomac Rivers export 23 and 19 percent of anthropogenic nitrogen inputs to their watersheds (respectively), whereas the Rappahannock and James Rivers export only 11 percent of these inputs.

Decay processes in flowing and impounded streams significantly limit the transport of nutrients from the Chesapeake Bay watershed to tidal waters. Comparison of local and delivered yields (fig. 9) illustrates that delivery of nitrogen from much of the Susquehanna watershed is relatively efficient (near 100 percent); more significant aquatic nitrogen losses in the Potomac watershed and further south reflect the importance of temperature to aquatic decay of nitrogen in large rivers (table 1). The greatest local nitrogen yields in the Chesapeake Bay watershed (outside of catchments affected by large point sources) occur in the predominantly agricultural areas of the Shenandoah Valley, the Great Valley, and Piedmont in Pennsylvania and central Maryland, and on the Delmarva Peninsula (fig. 9a). Much of this nitrogen is lost along streams, particularly in the upper Potomac watershed, however. The greatest yields of nitrogen delivered to Chesapeake Bay are contributed from agricultural areas of the northern Piedmont and Valley and Ridge, areas from which cooler temperatures and (or) close proximity limit nitrogen losses during fluvial transport to the bay (fig. 9b). Unlike nitrogen, however, local and delivered yields of phosphorus are very similar for much of the Chesapeake Bay watershed (fig. 10). Aquatic decay in the TP model is limited to impoundments, and predicted phosphorus delivery through the stream network is close to 100 percent in many areas, even from the Susquehanna watershed. Reservoirs behind the Safe Harbor and Holtwood Dams on the lower Susquehanna River have reached their capacity for retaining sediment and attached phosphorus (Hainly and others, 1995), and the SPARROW model suggests minimal phosphorus retention even in the downstream reservoir behind Conowingo Dam.

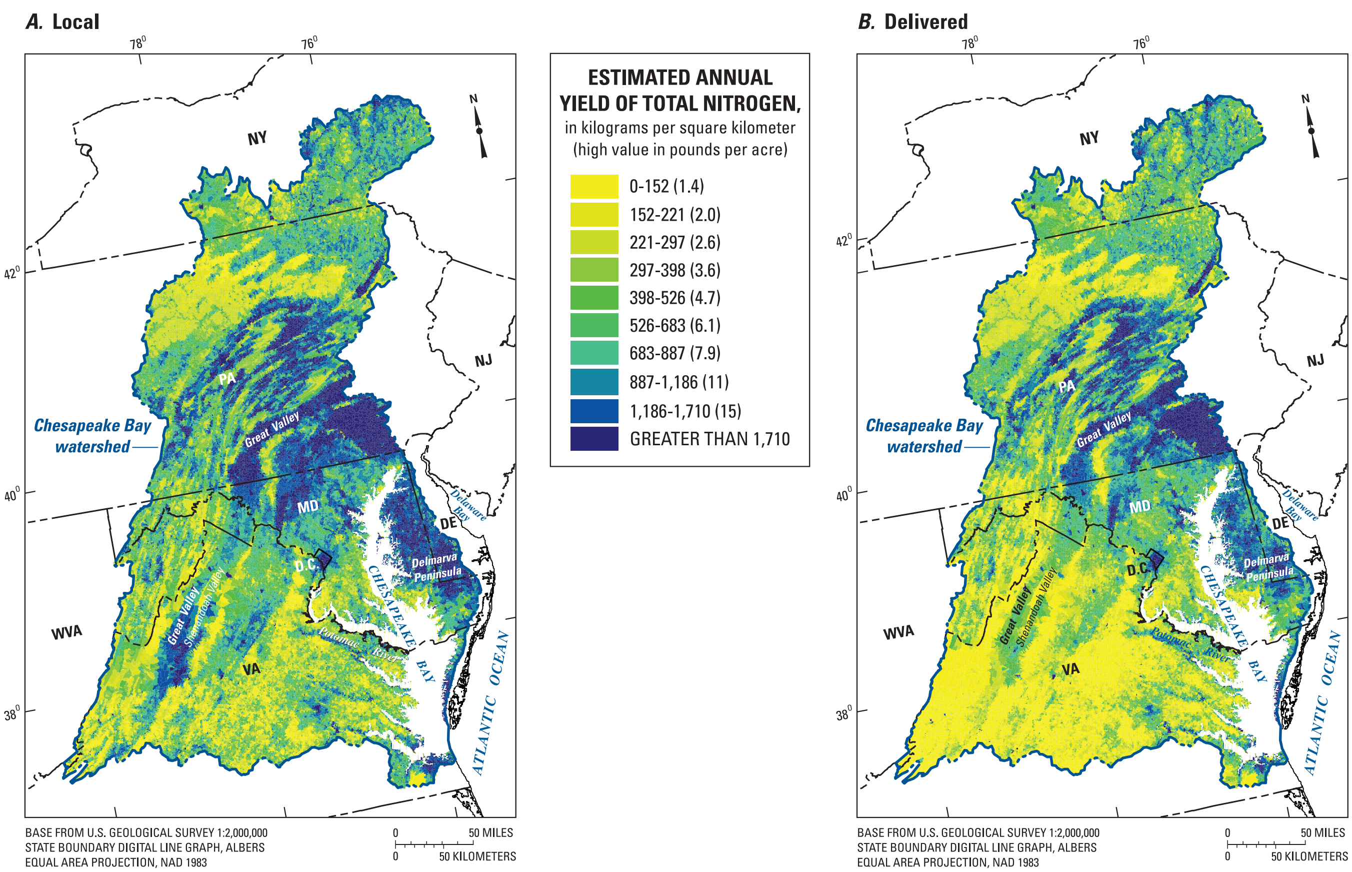

Figure 9. Estimated *(A)* local and *(B)* delivered yields of total nitrogen (TN). Local yields represent TN flux delivered to streams from individual local catchments; delivered yields represent TN flux delivered to downstream terminal reaches (generally tidal waters).

Flux to Chesapeake Bay and Major Tributaries

Watershed sources contribute an estimated 132,000 Mg (metric tons) (1.32×10^8 kg) of nitrogen and 9,740 Mg (9.74×10^6 kg) of phosphorus to the Chesapeake Bay and tidal tributaries annually (table 3). Because these estimates are based on SPARROW models calibrated to TN and TP flux during 2002 under long-term mean hydrologic conditions (see above), they represent the typical flux of nitrogen and phosphorus under such conditions. Actual nutrient fluxes vary considerably from year to year due to normal variability in weather (particularly precipitation) and streamflow (Langland and others, 2006). Nearly two-thirds (62 percent) of the nitrogen flux and nearly half (44 percent) of the phosphorus flux from the watershed to the bay during mean weather conditions is contributed by the combined flow of the Susquehanna and Potomac Rivers; 45 percent of the nitrogen flux and 28 percent of the phosphorus flux is contributed by the Susquehanna River alone (table 3).

Nitrogen contributions to Chesapeake Bay from the watershed are attributable primarily to agriculture. The combination of manure and fertilizer applications and fixation by crops provides more than half (54 percent) of the estimated nitrogen contributions to the bay and the largest source of nitrogen in most major tributaries (fig. 11). In a wider study of nitrogen contributions to 34 estuaries in the eastern United States, Castro and others (2003) similarly estimated that 53 percent of nitrogen contributed to Chesapeake Bay is attributable to agricultural runoff. Boyer and others (2002) similarly estimated that agricultural fertilizer use and fixation by crops, alone, contributed between 38 and 58 percent of nitrogen inputs to the Susquehanna, Potomac, James, and Rappahannock watersheds in the early 1990s. Agriculture is common in many areas of the Chesapeake Bay watershed, particularly near tidal waters (such as on the Delmarva Peninsula) and along major tributaries (such as the Susquehanna River) where opportunities for nitrogen losses along the stream network are limited (fig. 1). Contributions of point sources and atmospheric deposition are much smaller (approximately 16 percent each) and undifferentiated urban sources contribute an additional 12 percent of total estimated nitrogen flux from the watershed to the bay (fig. 11).

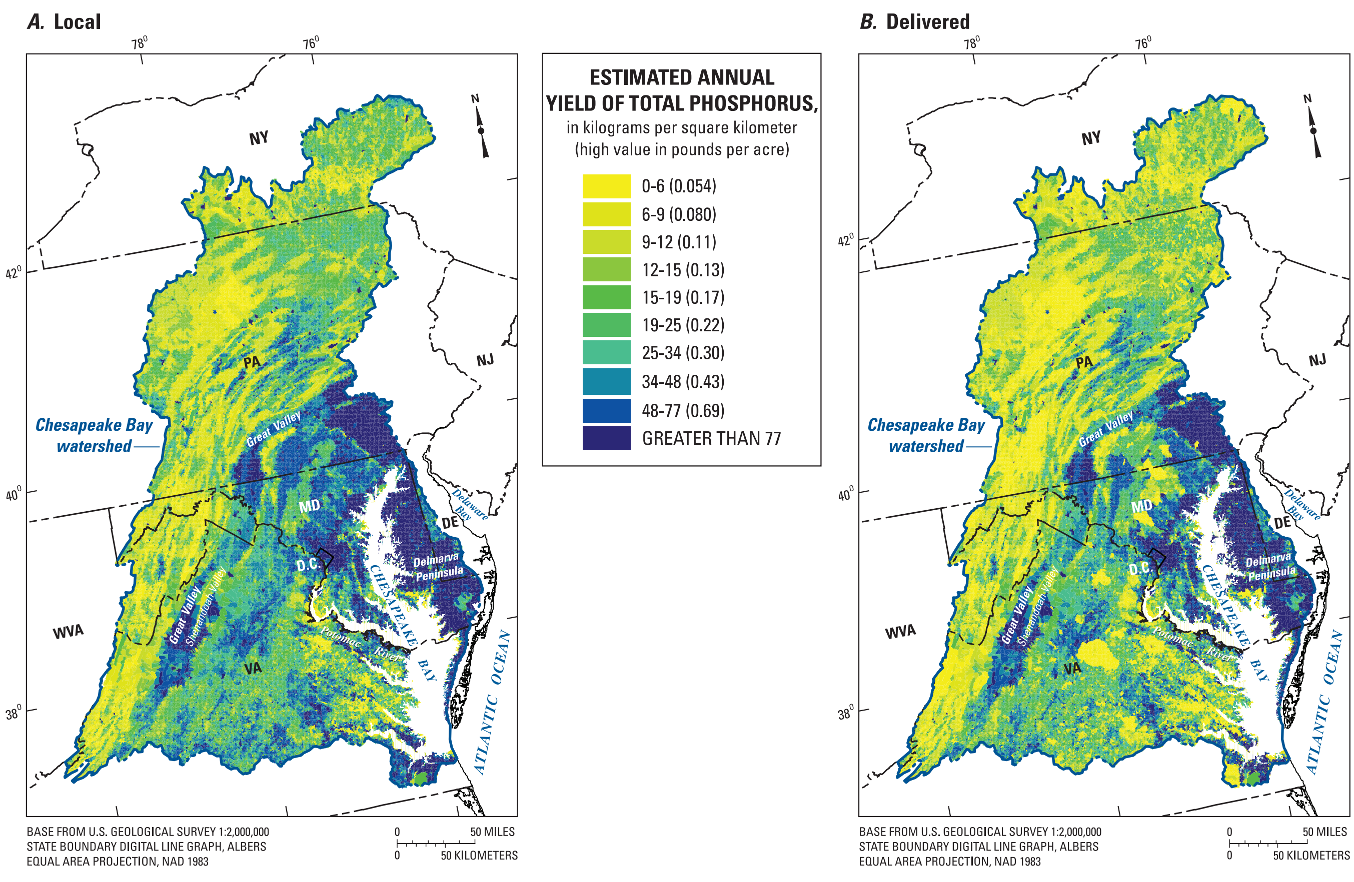

Figure 10. Estimated *(A)* local and *(B)* delivered yields of total phosphorus (TP). Local yields represent TP flux delivered to streams from individual local catchments; delivered yields represent TP flux delivered to downstream terminal reaches (generally tidal waters).

Table 3. Estimated annual flux of total nitrogen and total phosphorus from watershed sources to Chesapeake Bay and at selected monitoring stations on major tributaries, in metric tons.

[Mg, metric tons; Md., Maryland; Va., Virginia]

Chesapeake Bay or nontidal tributary[1] (station number)	Total Nitrogen (Mg)		Total Phosphorus (Mg)	
	CBTN_v4 model	Mean, 1990–2010[2]	CBTP_v4 model	Mean, 1990–2010[2]
Chesapeake Bay[3]	132,000		9,740	
Nontidal tributary (station number):				
1. Susquehanna River at Conowingo, Md. (01578310)	59,900	60,000	2,680	2,090
2. Potomac River at Washington, D.C. (01646580)	21,600	25,800	1,620	1,800
3. James River at Cartersville, Va. (02035000)	4,720	5,000	963	1,060
4. Rappahannock River near Federalsburg, Va. (01668000)	2,010	2,030	321	364
5. Appomattox River at Matoaca, Va. (02041650)	613	677	54.1	63.6
6. Pamunkey River near Hanover, Va. (01673000)	614	668	80.4	75.0
7. Mattaponi River near Beulahville, Va. (01674500)	259	284	22.9	25.9
8. Patuxent River near Bowie, Md. (01594440)	669	727	49.7	54.5
9. Choptank River near Greensboro, Md. (01491000)	219	222	15.3	13.6

[1] See figure 1 for locations.

[2] From U.S. Geological Survey, 2011b.

[3] Estimates include inputs to tidal tributaries, such as as from point sources and atmospheric deposition.

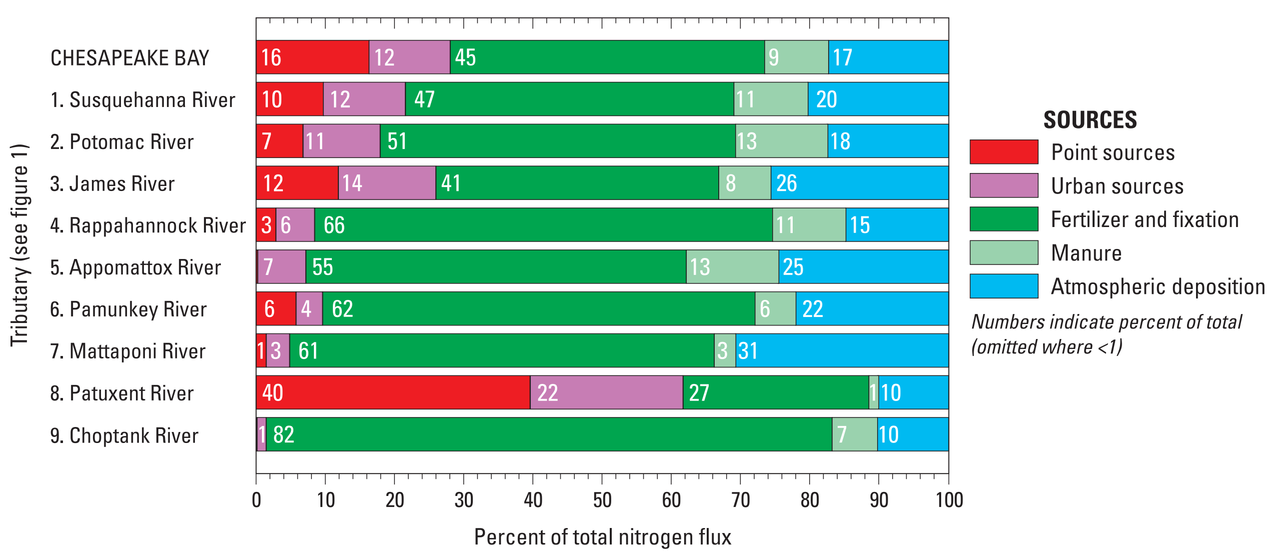

Figure 11. Estimated shares of total nitrogen contributions from various watershed sources to Chesapeake Bay and to major tributaries at selected monitoring stations.

The flux of phosphorus from the Chesapeake Bay watershed to the bay is contributed primarily from a mixture of urban and agricultural sources. Nearly half (43 percent) of the phosphorus reaching the bay is contributed from upstream agricultural fertilizer and manure applications; a nearly equal flux is contributed from point sources and other indistinguishable urban sources (fig. 12). The remainder (14 percent) of phosphorus contributed to the bay is from natural sources, including minerals in siliciclastic and crystalline rocks.

Summary and Implications

Spatially Referenced Regression On Watershed Attributes (SPARROW) modeling was used to provide quantitative empirical estimates of the sources, fate, and transport of nitrogen and phosphorus within the Chesapeake Bay watershed and to estimate mean annual total nitrogen (TN) and total phosphorus (TP) flux to the bay and in each of more than 80,000 tributary stream reaches represented in the NHDPlus (1:100,000-scale) geospatial dataset. The models were calibrated to mean annual TN and TP fluxes during 2002 in 181 and 184 watershed streams (respectively) that were estimated on the basis of available long-term nutrient and streamflow monitoring. Because the models were calibrated to estimated TN and TP flux during 2002 under long-term mean hydrologic conditions, they represent such long-term average conditions, rather than weather and resulting hydrologic conditions in any particular year.

Human sources contribute substantially to the nitrogen and phosphorus flux to Chesapeake Bay and major tributaries. Significant (α=0.10) sources of nutrients in the watershed include (primarily municipal) point sources, undifferentiated urban activities, and fertilizer and manure applications in agricultural areas. Additional significant sources of nitrogen include atmospheric deposition and direct fixation by crops; significant natural sources of phosphorus in Chesapeake tributaries include minerals in siliciclastic and crystalline rocks. Empirical estimates of average yields from source areas and proportions of selected applications transported to streams agree closely with previous estimates reported in the literature.

The fate and transport of nitrogen and phosphorus from source areas to streams and within the stream network are affected by natural hydrogeologic and soil conditions and by the distribution of impoundments (lakes, ponds, and reservoirs) in the watershed. Greater TN flux in areas of greater groundwater recharge (and presumably, discharge) and in areas underlain by selected carbonate rocks reflects the importance of groundwater to nitrogen transport (as nitrate) in the watershed, and the previously documented greater nitrate concentrations in streams and groundwater of carbonate areas. The importance of plant uptake and redox conditions to nitrate stability and fate in groundwater and streams is likely reflected in the significance of enhanced vegetative index (EVI) and soil available water capacity (AWC) (respectively) as land-to-water terms in the TN model. Nitrogen losses within impounded streams are likely due primarily to denitrification; losses within flowing streams are greatest in streams with mean annual flow less than 3.45 m^3 s^{-1} (cubic meters per

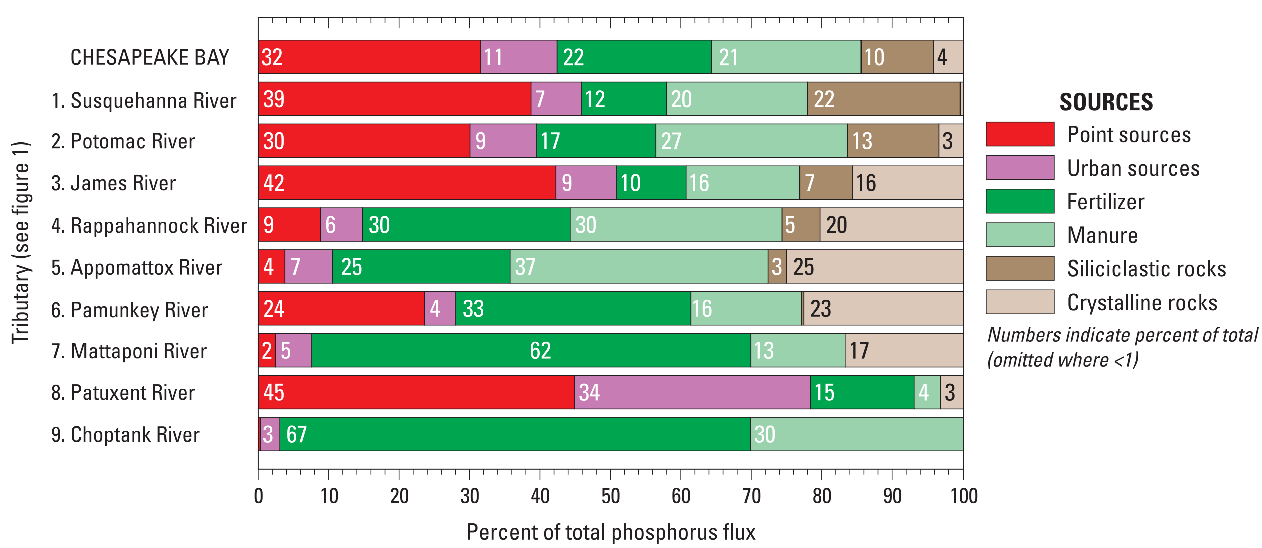

Figure 12. Estimated shares of total phosphorus contributions from various watershed sources to Chesapeake Bay and to major tributaries at selected monitoring stations.

second) (122 cubic feet per second), and in larger streams in warmer areas. Phosphorus transport from source areas to streams is greatest in areas where increased runoff and erosion are likely; the significance of the Coastal Plain to phosphorus transport may reflect soil saturation of phosphorus from previous applications in that setting. Phosphorus losses occur within impounded streams and rivers, but losses in flowing reaches are on average statistically insignificant.

Results from the TN and TP SPARROW models provide regional insight on nutrient sources and movement within the Chesapeake Bay watershed that can be particularly useful for management and restoration efforts. Along with estimated local and delivered mean annual TN and TP fluxes for each of more than 80,000 streams, the models provide empirically derived source shares and transport factors that provide insight into the most important processes in different areas and the most effective management strategies for different restoration goals.

Reducing nutrients from human sources could be particularly effective at limiting nitrogen and phosphorus flux from the watershed to the bay. Natural sources of nutrients occur in the watershed and provide the majority of relatively low nutrient fluxes from certain areas; more than 10 percent of total phosphorus flux to the bay is attributable to mineral sources. Human activities constitute the major sources of nutrients from the watershed to the bay, however, and the greatest potential for nutrient reductions. Agriculture, for example, contributes more than half of the nitrogen reaching the bay. Most of the agricultural nitrogen is derived from fertilizer applications and fixation by crops, and 24 percent of nitrogen from these sources does not contribute to crop growth, but rather is lost to streams. Precision applications or other techniques designed to limit fertilizer applications while maintaining crop yields may be particularly effective at limiting nitrogen flux to the Chesapeake Bay. Phosphorus is generally less mobile in the environment than nitrogen compounds and applied phosphorus is likely to be sequestered in terrestrial environments such as soils. Point sources discharging directly to streams provide approximately one-third of the phosphorus reaching the bay, and nearly half of the flux in some major tributaries. Reducing point sources may be more effective at limiting the overall flux of phosphorus than of nitrogen to Chesapeake Bay.

A review of regionally significant factors affecting nutrient fate and transport in the bay watershed could be useful, along with source descriptions for targeting management resources to specific areas. Regardless of sources, phosphorus transport is more efficient in areas where surface runoff is more likely, including areas with more erodible soils, relatively poor drainage, and greater precipitation. Similarly, nitrogen transport is most efficient in areas with greater groundwater recharge, certain carbonate rocks, and less reducing conditions that may contribute to denitrification. Targeting restoration activities to areas most likely to deliver nitrogen or phosphorus to streams may be useful alternatives if limiting applications or other sources is overly costly or otherwise difficult. Nutrient losses also occur within the aquatic system. Nitrogen loss rates are generally greater in smaller streams, and in larger streams in warmer areas of the watershed. Both nitrogen and phosphorus fluxes are decreased in impounded streams; nitrogen loss is likely due mainly to denitrification, whereas phosphorus attached to sediment particles may be lost to settling. These different loss processes may have important implications for restoration efforts, as nitrogen is lost permanently to the atmosphere through denitrification, whereas much of the phosphorus is merely stored in impoundments and may be remobilized in the future. Consideration of these aquatic losses is also important when balancing restoration goals for local streams with those of downstream receiving waters such as Chesapeake Bay.

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Appendix. Reach-Scale Estimates of Mean-Annual Nitrogen and Phosphorus Fluxes in Streams of the Chesapeake Bay Watershed

Mean annual total nitrogen (TN) and total phosphorus (TP) fluxes predicted by version 4 of the Chesapeake Bay SPARROW TN model (CBTN_v4) and TP model (CBTP_v4) are available online in a tab-delimited ASCII file at *http://pubs.usgs.gov/sir/2011/5167/CBTNTP_v4_predict.txt*. Variables in the online file are described in the header (denoted by lines starting with “#”), and include selected characteristics of the NHDPlus-based model network, as well as estimates of total and local (incremental) flux for each model reach and the fraction of local flux from each catchment that is delivered to downstream terminal reaches, which generally represent tidal waters. The file includes predictions for 81,908 individual stream reaches within the Chesapeake Bay watershed as defined by the National Hydrography Dataset Plus [NHDPlus, mid-Atlantic region (02)] medium resolution (1:100,000-scale) geospatial dataset (Horizon Systems, 2010), including 80,579 reaches representing nontidal tributaries and 1,329 reaches representing centerlines of tidal parts of major Chesapeake tributaries. These reaches can be identified by the variable, TIDAL_CHANNEL. Although SPARROW is not designed for modeling tidal waters, predictions for these 1,329 reaches can be used to estimate the total flux of TN or TP to Chesapeake Bay or tidal tributaries (including from sources contributing directly to tidal waters), but are not intended for other purposes. Stream decay was not applied to centerline tidal reaches for the purpose of these estimates; stream decay is calibrated in the SPARROW models to flowing reaches and is not intended to represent nutrient losses in tidal waters.

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