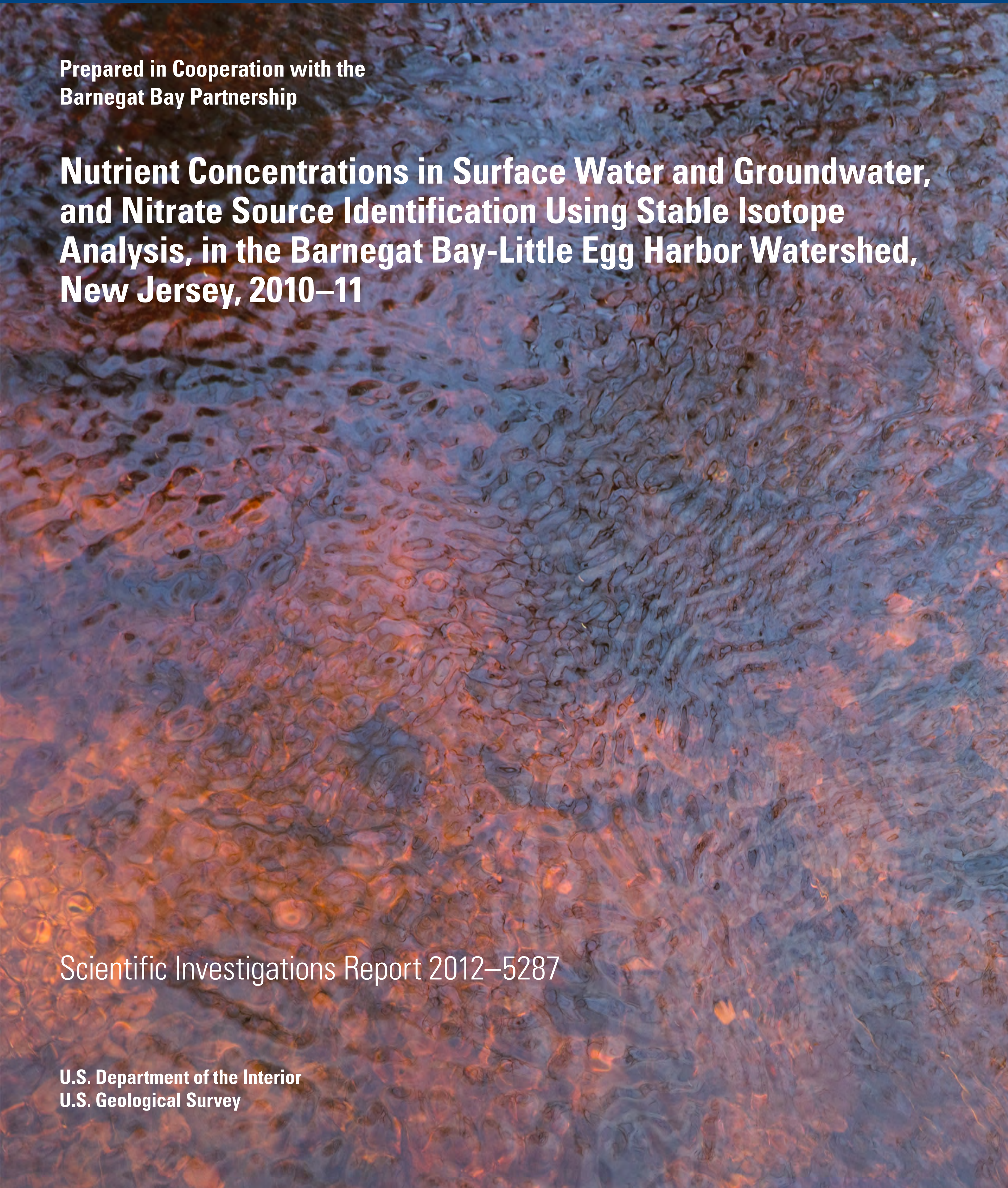

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Scientific Investigations Report 2012–5287

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

Cover: Photo of tea-colored water of Westecunk Creek, Ocean County, New Jersey. (Photograph by Robert Stern)

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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)	247.1	acre
square kilometer (km^2)	0.3861	square mile (mi^2)
	Flow rate	
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
cubic meter per second (m^3/s)	22.83	million gallons per day (Mgal/d)

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

°F=(1.8×°C)+32

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

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

Nutrient Concentrations in Surface Water and Groundwater, and Nitrate Source Identification Using Stable Isotope Analysis, in the Barnegat Bay-Little Egg Harbor Watershed, New Jersey, 2010–11

By Christine M. Wieben, Ronald J. Baker, and Robert S. Nicholson

Abstract

Five streams in the Barnegat Bay-Little Egg Harbor (BB-LEH) watershed in southern New Jersey were sampled for nutrient concentrations and stable isotope composition under base-flow and stormflow conditions, and during the growing and nongrowing seasons, to help quantify and identify sources of nutrient loading. Samples were analyzed for concentrations of total nitrogen, ammonia, nitrate plus nitrite, organic nitrogen, total phosphorus, and orthophosphate, and for nitrogen and oxygen stable isotope ratios.

Concentrations of total nitrogen in the five streams appear to be related to land use, such that streams in subbasins characterized by extensive urban development (and historical agricultural land use)—North Branch Metedeconk and Toms Rivers—exhibited the highest total nitrogen concentrations (0.84–1.36 milligrams per liter (mg/L) in base flow). Base-flow total nitrogen concentrations in these two streams were dominated by nitrate; nitrate concentrations decreased during storm events as a result of dilution by storm runoff. The two streams in subbasins with the least development—Cedar Creek and Westecunk Creek—exhibited the lowest total nitrogen concentrations (0.16–0.26 mg/L in base flow), with organic nitrogen as the dominant species in both base flow and stormflow. A large proportion of these subbasins lies within forested parts of the Pinelands Area, indicating the likelihood of natural inputs of organic nitrogen to the streams that increase during periods of storm runoff. Base-flow total nitrogen concentrations in Mill Creek, in a moderately developed basin, were 0.43 to 0.62 mg/L and were dominated by ammonia, likely associated with leachate from a landfill located upstream. Total phosphorus and orthophosphate were not found at detectable concentrations in most of the surface-water samples, with the exception of samples collected from the North Branch Metedeconk River, where concentrations ranged from 0.02 to 0.09 mg/L for total phosphorus and 0.008 to 0.011 mg/L for orthophosphate.

Measurements of nitrogen and oxygen stable isotope ratios of nitrate in surface-water samples revealed that a mixture of multiple subsurface sources, which may include some combination of animal and septic waste, soil nitrogen, and commercial fertilizers, likely contribute to the base-flow nitrogen load. The results also indicate that atmospheric deposition is not a predominant source of nitrogen transported to the BB-LEH estuary from the watershed, although the contribution of nitrate from the atmosphere increases during stormflow. Atmospheric deposition of nitrate has a greater influence in the less developed subbasins within the BB-LEH watershed, likely because few other major sources of nitrogen (animal and septic waste, fertilizers) are present in the less developed subbasins. Atmospheric sources appear to contribute proportionally less of the overall nitrate as development increases within the BB-LEH watershed.

Groundwater samples collected from five wells located within the BB-LEH watershed and screened in the unconfined Kirkwood-Cohansey aquifer system were analyzed for nutrient and stable isotope composition. Concentrations of nitrate ranged from not detected to 3.63 mg/L, with the higher concentrations occurring in the highly developed northern portion of the watershed, indicating the likelihood of anthropogenic sources of nitrogen. Isotope data for the two wells with the highest nitrate concentrations are more consistent with fertilizer sources than with animal or septic waste. Total phosphorus was not detected in any of the wells sampled, and orthophosphate was either not detected or measured at very low concentrations (0.005–0.009 mg/L) in each of the wells sampled.

Introduction

The Barnegat Bay-Little Egg Harbor (BB-LEH) estuary is a shallow, lagoonal-type estuary located along the central coast of New Jersey, separated from the Atlantic Ocean by a narrow complex of barrier islands (Kennish, 2001). The estuary is composed of Barnegat Bay, Manahawkin Bay, and Little Egg Harbor (fig. 1). Historically, the estuary has been a vital economic and recreational resource, supporting both

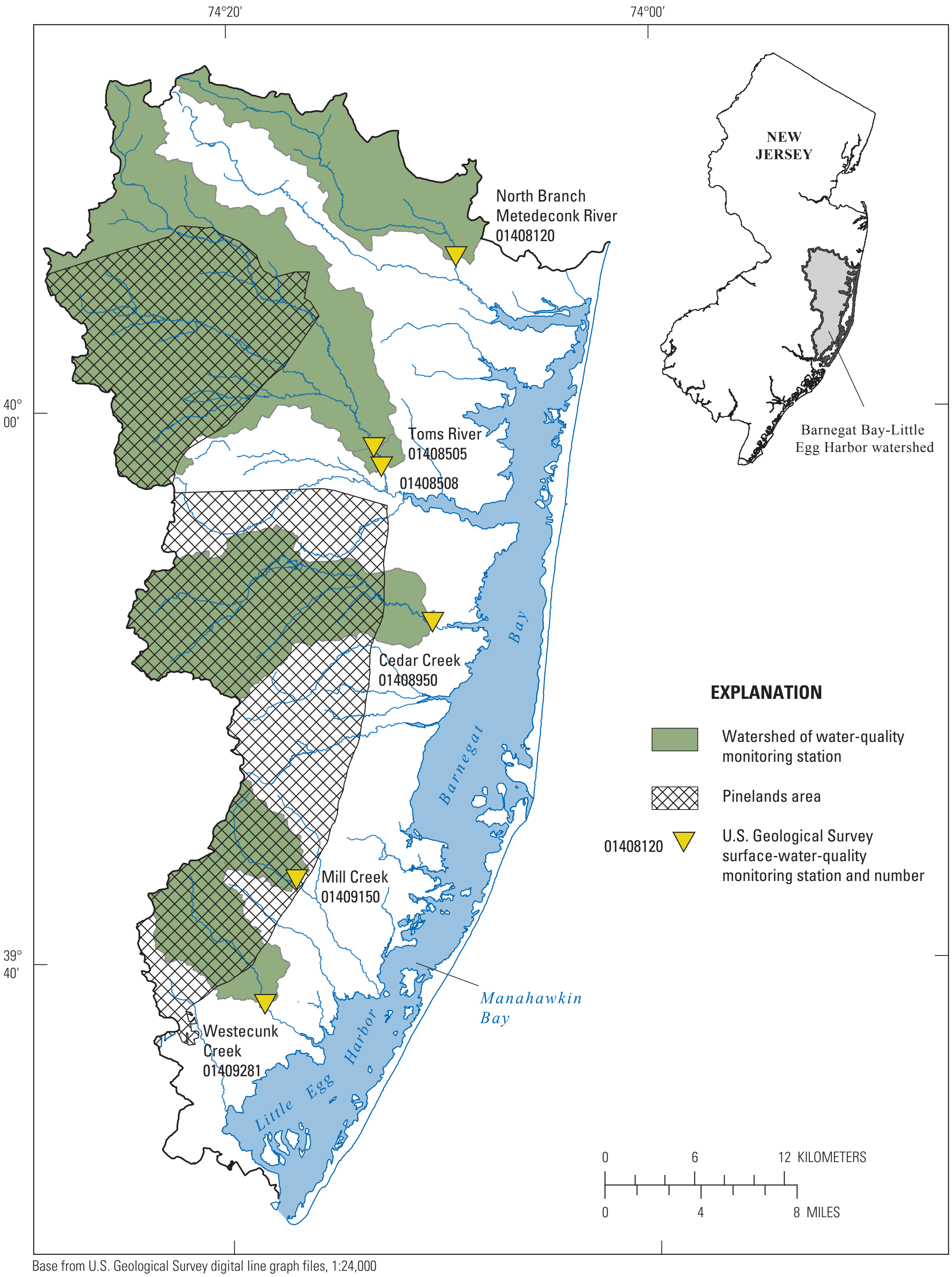

Figure 1. Barnegat Bay-Little Egg Harbor estuary and watershed with locations of selected surface-water-quality stations.

commercial and recreational fish and shellfish industries, as well as boating and tourism. The estuary and adjacent lands offer a variety of ecologically important habitats including sand beaches and dunes, salt marshes, submerged aquatic vegetation beds, shellfish beds, and waterfowl nesting grounds (Barnegat Bay National Estuary Program, 2002).

Physical characteristics of the estuary, including its shallow depth and limited outlets for exchange with ocean water (poor flushing), render it particularly susceptible to the effects of nutrient loading and, over the last few decades, the ecological health of the estuary has deteriorated (Kennish and others, 2007). In particular, the estuary has experienced increases in macroalgal growth, harmful algal blooms, and turbidity, as well as oxygen depletion, declines in harvestable fisheries, and changes in species composition, including decreases in the biomass and size of seagrass beds (Kennish and others, 2007). The estuary has been classified as highly eutrophic based on the National Oceanographic and Atmospheric Administration National Estuarine Eutrophication Assessment (Bricker and others, 1999; Bricker and others, 2007).

Nixon (1995) defined eutrophication as "an increase in the rate of supply of organic matter to an ecosystem," most commonly caused by nutrient enrichment. According to Liebig's Law of the Minimum, plant growth is limited by the availability of the scarcest resource, not by the total amount of resources available (von Liebig, 1855). Phosphorus is more often the limiting nutrient for plant growth in freshwater systems, whereas nitrogen is more often the limiting nutrient in estuaries and coastal ecosystems (Hecky and Kilham, 1988; Howarth, 1988). In the case of the BB-LEH estuary, nitrogen is the primary limiting nutrient for plant growth, but secondary limitation by phosphorus occurs during periods of high nitrogen loading (Seitzinger and others, 2001). As a result, eutrophication can be controlled by restricting the loading of the primary limiting nutrient (Smith and Bennett, 1999), either by reducing nitrogen inputs to the estuary or by increasing the flushing rate of water in the estuary in order to decrease the frequency and severity of adverse effects attributable to eutrophication.

Most point sources of nutrients (for example, municipal and industrial discharges from waste-water treatment facilities) have been eliminated from the BB-LEH watershed. Therefore, the main contributors of nutrients and other water-quality constituents to the BB-LEH estuary are nonpoint sources (NPSs). Constituents from NPSs are transported to streams that feed the estuary by groundwater and by surface (storm) runoff from diffuse areas or from areas where sources of constituents are not easily identified or quantified (Baker and Hunchak-Kariouk, 2006). NPS discharges include surface runoff from agricultural, residential, and nonresidential developed areas; leachate from septic systems, underground storage tanks, and landfills transported by groundwater; and atmospheric deposition. NPS contributions to a surface-water body are greatly influenced by land use—both current and historical—within a subbasin. NPS constituents transported to a surface-water body by surface runoff generally are attributed to current land use, whereas NPS constituents transported to a surface-water body through groundwater may be attributed to either current or historical land use, depending on flow paths and recharge rates in the contributing drainage area. For example, nitrate from agricultural activities can be discharged into streams many years after farmland has been converted to urban development, as shown by Kauffman and others (2001).

Source identification of nitrogen in the watershed is fundamental to developing and prioritizing plans to reduce nitrogen inputs to the estuary. Nitrate (NO_3^-) is commonly the most abundant form of dissolved nitrogen in both surface water and shallow groundwater. Measurements of nitrogen and oxygen isotope ratios (^{15}N:^{14}N and ^{18}O:^{16}O, respectively) of NO_3^- in water samples can be used in combination with water-chemistry and hydrologic data to help identify the predominant sources of nitrate, and subsequently nitrogen, to the estuary—whether it be from atmospheric, inorganic-fertilizer, animal- and septic-waste, or natural sources (Kendall and others, 2007). Nitrogen and oxygen isotope ratios are reported as delta (δ) values in units of parts per thousand (denoted as ‰, or per mil) of ^{15}N or ^{18}O higher or lower than an international reference standard. The δ values are computed as

$$\delta^{15}N \text{ or } \delta^{18}O = (R_{sample}/R_{standard} - 1) * 1{,}000 \quad , \qquad (1)$$

where

R_{sample} and $R_{standard}$ represent the ratios of ^{15}N:^{14}N and ^{18}O:^{16}O in the sample and standard, respectively.

The $\delta^{15}N$ values are reported relative to the ratio in atmospheric air, and the $\delta^{18}O$ values are reported relative to the Vienna Standard Mean Ocean Water (VSMOW) ratio; both reference standards have defined δ values of 0 ‰ (Kendall and others, 2007).

Kendall and others (2007) described the characteristic nitrogen and oxygen isotope compositions of the various sources of nitrate (fig. 2). Reported $\delta^{15}N$ values of nitrate that derive from animal and septic waste span a wide range (0 to +25 ‰) but are typically at the higher end of the range (+10 to +20 ‰) as a result of ammonia volatilization preceding nitrification. The $\delta^{15}N$ values from synthetic nitrate fertilizer samples are commonly within a few per mil of zero, whereas those from nitrate that was applied as ammonium fertilizer and subsequently nitrified have a broader range (-10 to +5 ‰). Most soil nitrate (formed from the oxidation of organic matter) has a $\delta^{15}N$ value of +2 to +5 ‰ (Kendall, 1998), but the $\delta^{15}N$ values tend to be higher when the nitrate is derived from animal waste. The $\delta^{15}N$ values for atmosphere-derived nitrate span a wide range (-15 to +15 ‰). When a multi-isotope approach is used, $\delta^{18}O$ values can be used to further differentiate among nitrate sources. The $\delta^{18}O$ values from synthetic nitrate fertilizers exhibit a fairly narrow range (+17 to +25 ‰); those for nitrate derived from ammonium fertilizers tend to be lower (less than +15 ‰), and those for atmospherically derived nitrate are consistently high (greater

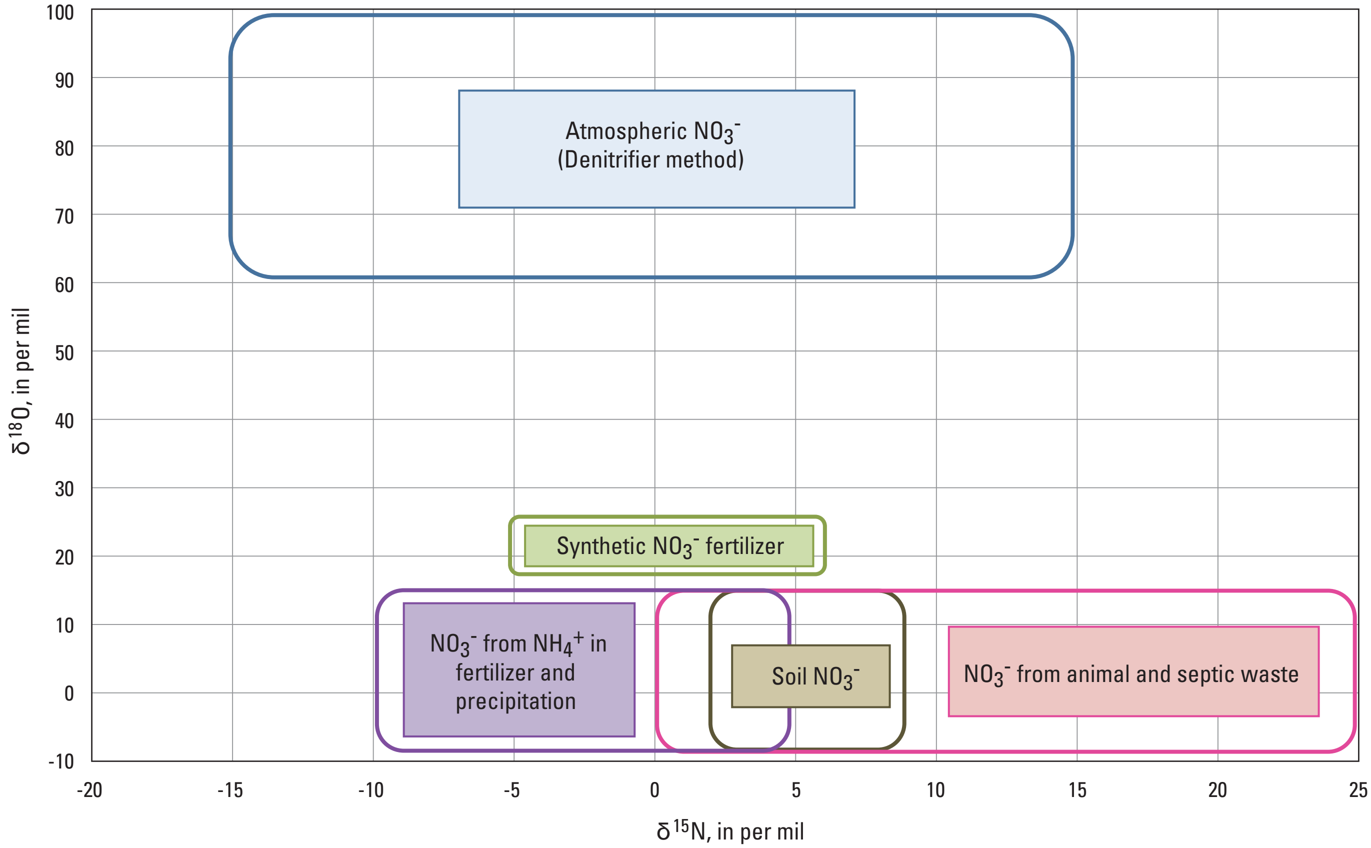

Figure 2. Typical ranges of $\delta^{15}N$ and $\delta^{18}O$ values of nitrate in water derived from atmospheric, fertilizer, soil, and septic and animal-waste sources. (Modified from Kendall and others, 2007; NO_3^-, nitrate; NH_4^+, ammonium)

than +60 ‰). Therefore, the combined use of nitrogen and oxygen isotope ratios can yield information about the sources of nitrogen to specific water bodies.

Generally, isotopic signatures of nitrate from different sources are brought about by the preferential use of lighter isotope fractions of oxygen and nitrogen in biological, physical, and chemical reactions. For example, during denitrification, the lighter isotope (^{14}N) is preferentially utilized, leaving a larger fraction of the heavier isotope (^{15}N) in the unreacted NO_3^-. Over time and distance in anoxic groundwater, denitrification can result in an increase in the $\delta^{15}N$ value of dissolved nitrate (while decreasing the total concentration of NO_3^-). Conversely, nitrification results in lower values of $\delta^{15}N$ in the nitrate than in the reactant ammonium.

Additional information about sources and cycling of nitrogen can be gained by relating $\delta^{15}N$ and $\delta^{18}O$ values to concentrations of dissolved solids, such as chloride, potassium, and sodium. For example, Silva (2002) reported that a positive correlation between $\delta^{15}N$ and chloride concentration in samples from two creeks near Austin, Texas, in conjunction with higher chloride concentrations and higher $\delta^{15}N$ values in the base-flow samples, is consistent with nitrate from a sewage source. Additionally, a plot showing decreasing dissolved-oxygen concentration with increasing $\delta^{15}N$ values in groundwater from unsewered areas and the absence of such a relation in sewered areas was evidence that nitrate in unsewered areas was contributed by septic systems. Relations between stable isotope ratios and concentrations of dissolved cations and anions were similarly examined in this study to help identify nitrogen sources and their relative importance in the BB-LEH watershed.

Previous and ongoing investigations have estimated rates of nitrogen and phosphorus input to the BB-LEH estuary by using limited available hydrologic and water-quality data. Although some inputs are well characterized (for example, tributaries to the Toms River), nutrient loading from groundwater and other streams in the watershed is not well known. More accurate determination of the spatial variability of nutrient loading throughout the watershed requires additional water-quality and hydrologic data. Data needs identified by Wieben and Baker (2009) that would improve the understanding of nutrient inputs to the estuary include surface-water-quality data collected during various seasons and under varying hydrologic conditions (base flow and stormflow) for major streams in the watershed; more recent surface-water- and groundwater-quality data for the southern portion of the BB-LEH watershed, particularly in areas that have experienced a substantial increase in urban development in recent years; and shallow groundwater-quality analyses near major streams and in the area that contributes direct groundwater discharge to the estuary, adjacent coastal wetlands, or minor coastal tributaries. Another data need identified is stable isotope analysis of nitrate in surface and groundwater to help identify sources of nitrogen to the estuary. This would close a critical data gap, and would provide information about the types of control measures that might be instituted to reduce nitrogen inputs and how to focus and prioritize such measures. In this investigation, these data gaps were addressed by the U.S. Geological Survey (USGS) in cooperation with the Barnegat Bay Partnership by collecting hydrologic, water-quality, and stable isotope data for major streams and representative groundwater wells in the BB-LEH watershed.

Purpose and Scope

This report describes the results of a study to determine the predominant sources of nutrients to the BB-LEH estuary. It includes data on streamflow and surface-water quality measured in samples collected from five streams or their tributaries that discharge to the estuary—North Branch Metedeconk River, Toms River, Cedar Creek, Mill Creek, and Westecunk Creek—from March to October 2010. Surface-water-quality samples were collected during periods of base flow and stormflow in the growing and nongrowing seasons. Although surface-water samples were collected during only two precipitation events, water-quality and stable isotope data collected during this investigation, in combination with data collected previously, provide an assessment of ranges of nutrient concentrations in the five streams that together drain more than 40 percent of the BB-LEH watershed. The first sampling event occurred during a major precipitation event in the nongrowing season, from March 12 to15, 2010, following a wet winter. More than 5 inches of rain fell on parts of the watershed, and the highest peak flow in 81 years of record was recorded at the Toms River near Toms River, New Jersey, continuous-record streamflow-gaging station (U.S. Geological Survey, 2010). The second sampling event occurred during the growing season, from September 27 to October 1, 2010, when more than 2.5 inches of rain fell on parts of the watershed. This event followed an extended dry period throughout much of New Jersey, and streamflows in the study area were considerably lower than during the first storm event. Water-quality samples were collected before and during each storm so that water-quality data could be obtained for a variety of flow conditions. The water-quality constituents for which concentrations are reported are total nitrogen, nitrate plus nitrite, ammonia, organic nitrogen, total phosphorus, and orthophosphate; nitrogen and oxygen stable isotope ratios of nitrate in surface-water samples also are presented.

This report also provides water-quality and stable isotope ratio data for five wells located within the BB-LEH watershed collected from August 2010 to April 2011. These data are useful in quantifying concentrations of nutrients that are discharged from the subsurface to streams in the watershed and directly to the estuary.

Description of Study Area

The study area lies entirely within the Atlantic Coastal Plain physiographic province and includes the drainage basins of five streams, or their tributaries, that discharge to the BB-LEH estuary—North Branch Metedeconk River, Toms River, Cedar Creek, Mill Creek, and Westecunk Creek.

Predominant land uses within the BB-LEH watershed vary regionally (fig. 3). The northeastern mainland area is highly developed, with both residential and nonresidential development, and includes major population centers such as Toms River and Lakewood. The southeastern mainland area contains several protected wildlife refuge and wildlife management areas and is less heavily developed than the northeastern portion of the watershed; however, this area has undergone a substantial increase in development in recent years. The complex of barrier islands on the eastern shore of the estuary is heavily developed, with the exception of Island Beach State Park. Much of the western portion of the watershed lies within the Pinelands Area; this area is protected under the Pinelands Comprehensive Management Plan and is characterized by large tracts of forested land and some low-density development (Kennish, 2001; Hunchak-Kariouk and Nicholson, 2001).

The percentage of land in each land-use category was quantified for the BB-LEH watershed and for each of the five subbasins, on the basis of the 2007 land-use/land-cover digital dataset produced by the New Jersey Department of Environmental Protection (2010) (table 1). For the purpose of this report, residential development was distinguished from nonresidential development (commercial, industrial, and transportation-related areas, and military installations). The distribution of land use in 2007 within the entire BB-LEH watershed was 39.1 percent forested, 24.7 percent wetlands, 22.3 percent residential development, 7.9 percent nonresidential development, 2.7 percent water, 2.1 percent barren land, and 1.2 percent agriculture. The headwaters of the Toms River, Cedar Creek, Mill Creek, and Westecunk Creek are in the Pinelands Area (fig. 1).

The five subbasins differ in size and extent of development (table 1). The North Branch Metedeconk River subbasin upstream from the sampling station (the northernmost subbasin) covers 89.4 square kilometers (km^2) and is the most heavily developed. Approximately 42 percent of the land cover upstream from the sampling station is developed, most (80 percent) of which is residential. Approximately 20 percent of the subbasin is forested, and 5.2 percent is used for agriculture.

The Toms River subbasin upstream from the sampling station extends over 323.6 km^2 and is the largest of the subbasins studied. Approximately 25 percent of the subbasin is developed (residential, military installation, and other nonresidential development), 44 percent is forested, and 2.4 percent is

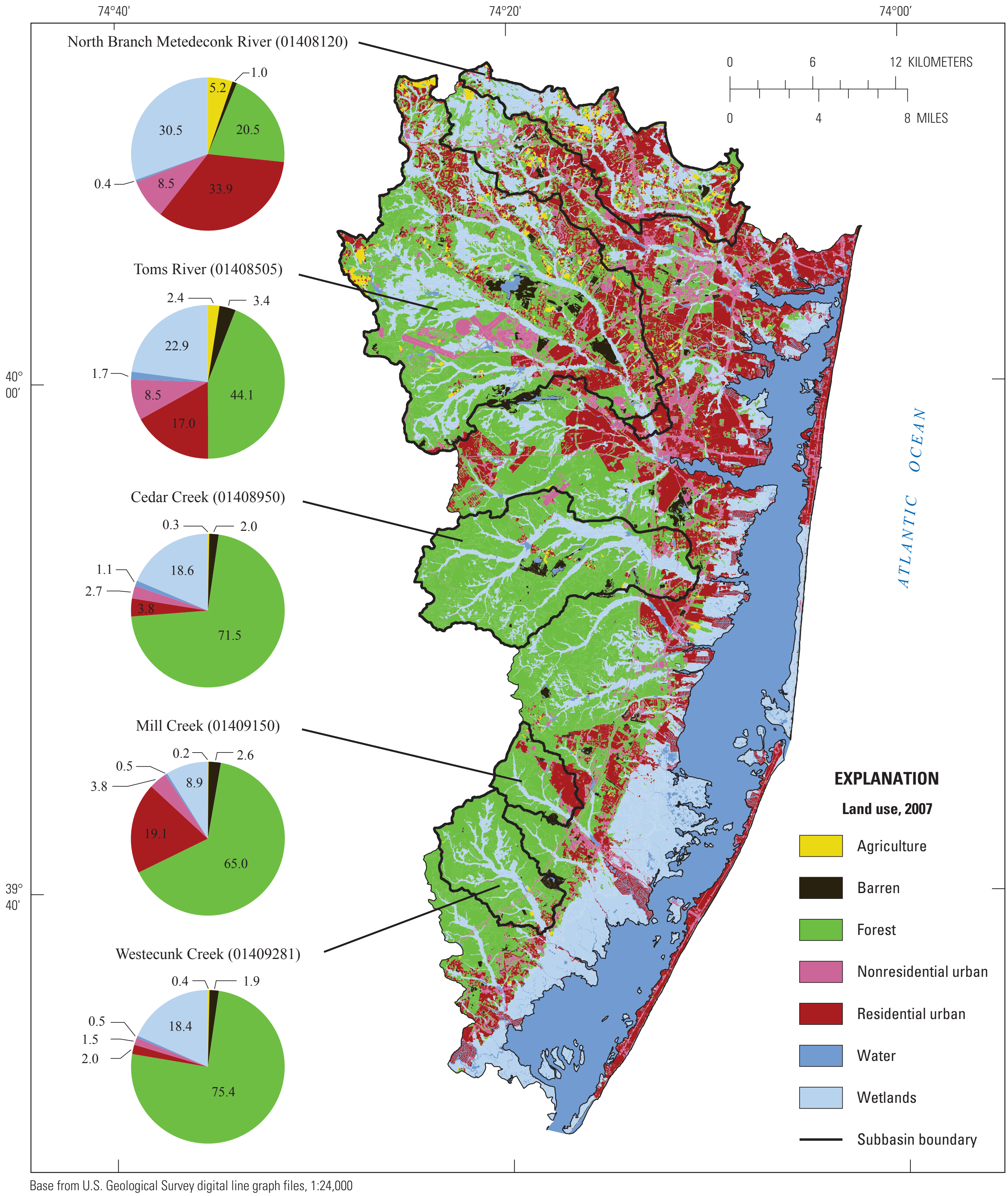

Figure 3. Land use in the Barnegat Bay-Little Egg Harbor watershed, 2007. (Land use from the New Jersey Department of Environmental Protection digital data file, 2010; pie charts show land use as a percentage of subbasin area; nonresidential urban land use includes commercial, industrial, and transportation related areas, and military installations.)

Table 1. Land-use distributions for selected subbasins of the Barnegat Bay-Little Egg Harbor watershed, 2007.

[Land use from New Jersey Department of Environmental Protection digital data file, 2010; RR, railroad; totals of land-use percentages may not equal 100.0 percent due to rounding]

U.S. Geological Survey station number	Station name	Drainage area, in square kilometers	Percentage of subbasin in the Pinelands Area	Land use, in percentage of drainage area					
				Agriculture	Barren land	Forest	Residential urban	Nonresidential urban[1]	Wetlands and water
01408120	North Branch Metedeconk River near Lakewood, NJ	89.4	0.0	5.2	1.0	20.5	33.9	8.5	30.9
01408505	Toms River at park footbridge, near Toms River, NJ	323.6	56.6	2.4	3.4	44.1	17.0	8.5	24.6
01408950	Cedar Creek at abandoned RR bridge, near Lanoka, NJ	136.1	89.3	0.3	2.0	71.5	3.8	2.7	19.7
01409150	Mill Creek near Manahawkin, NJ	26.6	100.0	0.2	2.6	65.0	19.1	3.8	9.4
01409281	Westecunk Creek at Railroad Ave, at West Creek, NJ	53.3	80.3	0.4	1.9	75.4	2.0	1.5	18.9

[1]Nonresidential urban land use includes commercial, industrial, and transportation-related areas, and military installations.

used for agriculture. More than 50 percent of the subbasin lies within the Pinelands Area.

The Cedar Creek subbasin upstream from the sampling station covers 136.1 km^2 and is primarily undeveloped. Nearly 90 percent of the subbasin lies within the Pinelands Area, and more than 70 percent is forested. Approximately 6.5 percent of the subbasin is developed; most development is in the lower one-fifth of the subbasin and is a mix of residential and nonresidential development. Less than 0.5 percent of the subbasin is used for agriculture.

The Mill Creek subbasin upstream from the sampling station covers 26.6 km^2 and lies entirely within the Pinelands Area. About 65 percent of the subbasin is forested, 23 percent is developed, and less than 0.5 percent is agricultural land. Most of the development is residential and is located primarily north of Route 72.

The southernmost subbasin, Westecunk Creek, covers 53.3 km^2 upstream from the sampling station and is the least developed of the subbasins. Seventy-five percent of the subbasin is forested, and less than 4 percent, most of which is downstream from the Pinelands Area boundary, is developed. Less than 0.5 percent is agricultural land.

The shallow, unconfined Kirkwood-Cohansey aquifer system underlies most of the BB-LEH watershed and thickens downdip to the southeast (Zapecza, 1989). The Cohansey Formation is composed primarily of medium- to coarse-grained sands, with localized occurrences of silt and clay lenses and gravel. The Kirkwood Formation is composed of fine- to medium-grained sands with clay and, to a lesser extent, coarse to fine gravelly sand (Canace and Sugarman, 2009). The sands and gravels of this aquifer system make it an excellent source of water supply for communities within the watershed; however, the Kirkwood-Cohansey aquifer system is highly susceptible to contamination from human activity because it generally lacks an overlying confining layer to impede the downward movement of contaminants originating at the land surface (Watt, 2000). In addition, the predominance of highly permeable unconsolidated sands and gravels facilitates the migration of contaminants from the land surface to the aquifer system (Stackelberg and others, 1997).

Some groundwater enters the BB-LEH estuary as direct seepage through estuarine sediments, but most groundwater discharges from the Kirkwood-Cohansey aquifer system to major streams in the watershed, including the Toms and Metedeconk Rivers, and to other, smaller streams and tributaries with eventual release to the estuary. Streams, wetlands, and other surface-water bodies are hydraulically well connected with the Kirkwood-Cohansey aquifer system; consequently, groundwater discharge from the aquifer system accounts for a high percentage (71–93 percent) of surface-water flow in the watershed and is the largest source of freshwater input to the BB-LEH estuary (Watt and others, 1994; Gordon, 2003; Nicholson and Watt, 1997).

Previous Studies

Both national- and local-scale studies have focused on nutrient concentrations in surface and groundwater. Nutrient concentrations in surface- and groundwater samples were compiled from water-quality assessments conducted across the United States from 1992 through 2001 in 51 major study units of the USGS's National Water-Quality Assessment (NAWQA) Program (Dubrovsky and others, 2010). Concentrations of total nitrogen were highest in streams in agricultural areas (median, 3.8 milligrams per liter (mg/L)) and urban areas (median, 1.5 mg/L). Total nitrogen concentrations downstream from relatively undeveloped watersheds generally were low. Concentrations of total phosphorus were elevated in streams in both agricultural and urban areas, with median concentrations of 0.26 and 0.25 mg/L, respectively. Concentrations of ammonia and orthophosphate were similar in streams in agricultural, urban, and mixed land-use areas. The relative abundance of different chemical forms of nitrogen in streams also is related to land use. For example, in streams in the northeastern United States, Pellerin and others (2004) found that concentrations of dissolved organic nitrogen increase as the percentage of wetlands in an area increases, whereas concentrations of dissolved inorganic nitrogen, which is typically dominated by nitrate, increase as the percentage of developed (agricultural plus urban) land increases.

Dubrovsky and others (2010) report that nitrate concentrations in groundwater were highest (median, 3.1 mg/L) in shallow wells beneath agricultural land, intermediate in shallow wells beneath urban land (median, 1.4 mg/L), and lowest in deep wells in major aquifers. The median concentration of nitrate was substantially higher in oxic groundwater (that is, water with dissolved-oxygen concentrations greater than 0.5 mg/L) than in groundwater without dissolved oxygen within each land-use setting. Wakida and Lerner (2005) determined that, under certain conditions, nitrate concentrations in groundwater that underlies urban areas can exceed those in groundwater beneath surrounding agricultural areas, citing leakage from sewage networks, on-site sewage disposal, animal waste, contaminated land, industrial processes, atmospheric deposition, urban fertilizer use, and house building as common nonagricultural sources of nitrogen to groundwater.

Trends in nutrient enrichment of rivers in the United States from 1975 to 1994 were reported by Alexander and Smith (2006). Among 250 streams studied (all with drainage areas greater than about 1,000 km^2), more streams showed decreases in flow-adjusted concentrations of total phosphorus and nitrogen than increases, with improvements attributed to wastewater-treatment upgrades, phosphate detergent bans, and declines in some agricultural sources. However, about 50 percent of all sites studied and more than 60 percent of sites in predominantly agricultural and urban watersheds were still classified as eutrophic. Similarly, Sprague and others (2009) analyzed trends in nutrient concentrations and loads in 244 streams across the United States from 1993 to 2003 and found that concentrations and trends at most of the sites did not change significantly during these years. However, a net upward flow-adjusted trend occurred at 33 percent of sites for total phosphorus, 21 percent for total nitrogen, and 12 percent for nitrate, potentially as a result of phosphorus saturation of soils in certain areas, and (or) lag time between anthropogenic changes on the land surface and changes in nutrient concentrations in streams.

On a local scale, several studies have focused on nutrient concentrations in groundwater and surface water in and near the BB-LEH watershed and on nutrient loading to the estuary. Nutrient concentrations representative of undisturbed areas of the New Jersey Outer Coastal Plain were provided in an investigation of the water quality in McDonalds Branch—a stream in a minimally developed basin located in the Pinelands Area immediately west of the BB-LEH watershed (Lord and others,1990; Johnsson and Barringer, 1993). In more than 80 surface-water samples, nitrate concentrations were mostly at or below the detection limit (0.04 or 0.44 mg/L, depending on the analytical method). In more than 200 groundwater samples, generally nitrate was either not detected or detected at less than 0.2 mg/L. This finding is consistent with that of Zampella (1994), who found that extremely low nutrient availability (typically the median nitrate plus nitrite concentration was less than 0.1 mg/L, and the median total phosphorus concentration was less than or equal to 0.03 mg/L) naturally characterizes the groundwater and surface-water geochemistry of the Pinelands hydrologic system (which spans southern and western portions of the BB-LEH watershed) and that nutrient concentrations (as well as pH and specific conductance) increased with increasing intensity of land use. Zampella and others (2007) investigated the relations between land-use patterns and water quality in the Mullica River Basin, which is immediately south of the BB-LEH Basin, and found that 10-percent altered land cover is the threshold at which a significant deviation from reference-site water-quality conditions occurs in the Mullica River Basin.

Kauffman and others (2001) used a groundwater-flow model with particle tracking to examine the effects of land use and travel time on the distribution of nitrate within a 400-square-mile (1,036 square kilometer) study area near Glassboro, New Jersey, southwest of the BB-LEH watershed. Simulation results showed that nitrate concentrations were highest in agricultural areas and lowest in largely undeveloped areas; that nitrate concentrations in the groundwater will remain elevated above background levels for decades even if nitrate inputs are immediately halted, as a result of the lag time associated with groundwater recharge; and that about 40 percent of the nitrate in aquifer recharge is lost to denitrification and in-stream processes.

Nicholson and others (2003) reviewed available water-quality data sets and reports for groundwater and surface water in or near the Metedeconk River, Toms River, and Kettle Creek Basins for 1980–2001. Results of analyses of untreated water samples collected from more than 13,000 private wells during 1983–99 indicated that concentrations of nitrate exceeded the Federal and New Jersey State drinking-water standard of 10 mg/L as nitrogen (N) in 0.5 percent of samples analyzed, according to records maintained by the Ocean County Health Department (Toms River, New Jersey). A similar analysis of more recent data also found that nitrate concentrations in 0.5 percent of wells sampled in 2005 exceeded 10 mg/L (Wieben, 2007). Trend tests conducted by Hickman and Barringer (1999) indicate that flow-adjusted concentrations of total nitrate plus nitrite increased at the Toms River surface-water-quality station during water years[1] 1986–95; no trend was identified for total phosphorus. The maximum concentration of total nitrate plus nitrite during this time period at the Toms River station was 0.95 mg/L (Hickman and Barringer, 1999). Although not a health risk in drinking water, concentrations of less than 1 mg/L NO_3^- as N can be substantial in an aquatic system and can contribute to eutrophic conditions. Trend tests conducted by Hickman and Gray (2010) for water years 1998–2007 indicate a continuing upward trend of dissolved nitrate plus nitrite concentrations at the Toms River station and a decreasing trend in total phosphorus concentrations.

Concentrations and loads of nutrient species in four tributaries to the Toms River were reported by Baker and Hunchak-Kariouk (2006). Water-quality and hydrologic data were collected over a 5-year period in four subbasins with different degrees of land development. Strong correlations were found between the percentage of land development and the loads of nutrients contributed by stormwater. Streams in subbasins with the least developed land had correspondingly lower concentrations of total nitrogen than streams in the moderate and highly developed subbasins.

Estimates of total nitrogen loads to the BB-LEH estuary were made by Hunchak-Kariouk and Nicholson (2001) and updated by Wieben and Baker (2009). Available data were used to quantify streamflow; average nitrogen concentrations during high- and low-flow conditions; and loading from surface water, groundwater, and atmospheric deposition. On the basis of the 2009 estimate, the total annual load of nitrogen to the BB-LEH estuary was calculated to be 650,000 kilograms (kg) N per year. Results of the study indicate that nitrogen transported to the estuary in surface water contributes 66 percent of the total nitrogen load, direct groundwater discharge contributes 12 percent, and direct atmospheric deposition to the estuary surface contributes 22 percent. Total nitrogen yields for basins in the more developed areas (greater than 10 percent developed) were about twice those for basins in less developed areas (less than 10 percent developed).

Stable isotope analysis has been developed to help identify sources of contaminants in surface-water and groundwater (Kendall and others, 2007; Fry, 2006). Aravena and others (1993) used stable nitrogen and oxygen isotope analysis to delineate a septic-system effluent plume in groundwater. The $\delta^{15}N$ values were substantially higher in the septic plume than in the surrounding groundwater, which had $\delta^{15}N$ values consistent with manure and synthetic fertilizer, and soil organic nitrogen. Additional information from $\delta^{18}O$ analysis showed that the presence of nitrate outside the plume is consistent with nitrification of ammonium and mineralization of organic nitrogen. Anisfeld and others (2007) used $\delta^{15}N$ and $\delta^{18}O$ analysis to estimate the fractions of nitrogen from sewage and atmospheric deposition reaching Long Island Sound from two rivers in Connecticut. The $\delta^{15}N$ values alone were too variable to make this estimation; however, the $\delta^{18}O$ values were useful for determining the contributions of nitrate from atmospheric deposition, and the combination of $\delta^{15}N$ and $\delta^{18}O$ results was used to quantify denitrification and determine the isotopic signature of sewage effluent for the study area. Cole and others (2006) monitored nitrogen loading and $\delta^{15}N$ values in groundwater seepage to ponds and estuaries on Cape Cod, Massachusetts. Areas with larger populations delivered larger nitrogen loads with higher $\delta^{15}N$ values. The differences among $\delta^{15}N$ values were strongly related to the density of septic systems, and much of the nitrogen load originated from nearshore (as opposed to inland) areas, implying attenuation of nitrogen upgradient from the discharge point.

[1] A water year is the 12-month period beginning October 1 of any given year and extending through September 30 of the following year. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 2007, is called the 2007 water year.

Methods

The following section describes the methods used to collect streamflow and water-quality data.

Streamflow Measurements

The U.S. Geological Survey (USGS) operates continuous streamflow-gaging stations on four of the five streams studied in this investigation—North Branch Metedeconk River, Toms River, Cedar Creek, and Westecunk Creek (table 2). Streamflow data for these stations were collected at 15-minute intervals using an electronic data logger and were retrieved from the USGS National Water Information System (NWIS), an online database. Additionally, manual (discrete) streamflow measurements were made on Mill Creek and Westecunk Creek during base flow and twice during stormflow, nearly concurrently with sample collection, to supplement the existing record because streamgages either were not present on the stream (Mill Creek) or were far from the sampling station (Westecunk Creek). These data are stored in NWIS. Streamgages were operated and streamflow records were computed in accordance with standard USGS protocols as described by Rantz and others (1982).

Water-Quality-Data Collection

Both surface-water and groundwater samples were collected and processed following standard USGS sampling protocols (U.S. Geological Survey, 2006). Samples were analyzed for concentrations of nitrogen and phosphorus species, for major cations and anions (including chloride, potassium, and sodium), and for nitrogen and oxygen stable isotope ratios. All samples except those collected for stable isotope analysis

Table 2. Information for selected streamflow-gaging stations in the Barnegat Bay-Little Egg Harbor watershed.

U.S. Geological Survey station number	Station name	Drainage area, in square kilometers	Period of record
01408120	North Branch Metedeconk River near Lakewood, NJ	89.4	1973-present
01408500	Toms River near Toms River, NJ	318.6	1929–66; 1967-present
01409000	Cedar Creek at Lanoka Harbor, NJ	138.0	1933–58; 1971; 2003-present
01409280	Westecunk Creek at Stafford Forge, NJ	40.9	1974–88; 2003-present

were analyzed at the USGS National Water Quality Laboratory in Denver, Colorado. Samples collected for stable isotope analysis were analyzed at the USGS Reston Stable Isotope Laboratory in Reston, Virginia. Detection and reporting levels for selected analytes are shown in table 3.

Field parameters measured at the time of sample collection included air temperature, water temperature, barometric pressure, pH, specific conductance, dissolved-oxygen concentration, and turbidity. Alkalinity was measured at the USGS New Jersey Water Science Center field laboratory in West Trenton, New Jersey, following sample collection.

Surface Water

Surface-water samples were collected at five sites (fig. 1) during periods of base flow and stormflow over the course of two sampling events. Each of the five surface-water sites was sampled three times during each event, yielding a total of 30 environmental samples for the surface-water portion of the study. The first sampling event occurred March 11–15, 2010, during the nongrowing season; the second sampling event occurred September 26–October 1, 2010, during the growing season. The dates of the growing season, April 1 to October 31, and nongrowing season, November 1 to March 31, were based on the average dates of the first and final frosts in New Jersey (Ruffner and Bair, 1977). Hydrographs were monitored by using real-time data from the continuous streamflow-gaging stations located within the Barnegat Bay-Little Egg Harbor (BB-LEH) watershed. Base-flow samples, represented by the pre-storm portion of the hydrograph, were collected prior to the anticipated storm event. The first set of stormflow samples was collected during the initial portion of the rising limb of the hydrograph to measure the concentration of constituents carried by streams during first flush (initial direct runoff). A second set of stormflow samples was collected near the peak of the hydrograph.

The streamgage and the water-quality sampling station on the North Branch Metedeconk River were collocated. As a result of concerns related to site accessibility and safety during storm sampling, the Toms River sampling station was located approximately 1.9 kilometers (km) downstream from the streamgage, the Cedar Creek sampling station was located

Table 3. Minimum detection and reporting levels for selected water-quality constituents.

[USGS, U.S. Geological Survey; mg/L, milligrams per liter; N, nitrogen; Cl, chloride; P, phosphorus; K, potassium]

Constituent	USGS parameter code	Range of dates	Minimum detection level	Minimum reporting level	Units
Ammonia	608	10/01/2009–09/30/2011	0.01	0.02	mg/L as N
Ammonia plus organic nitrogen	623	10/01/2009–09/30/2011	0.05	0.10	mg/L as N
Chloride	940	10/01/2009–09/30/2011	0.06	0.12	mg/L as Cl
Nitrate plus nitrite	631	10/01/2009–09/30/2011	0.02	0.04	mg/L as N
Nitrite	613	10/01/2009–09/30/2011	0.001	0.002	mg/L as N
Orthophosphate	671	10/01/2009–09/30/2011	0.004	0.008	mg/L as P
Potassium	935	10/01/2009–09/30/2010	0.032	0.064	mg/L as K
Potassium	935	10/01/2010–09/30/2011	0.022	0.044	mg/L as K
Total phosphorus	665	10/01/2009–09/30/2011	0.01	0.02	mg/L as P

approximately 0.6 km upstream from the streamgage, and the Westecunk Creek sampling station was located approximately 3.2 km downstream from the streamgage. On March 15, 2010, flood waters prevented access to the original Toms River sampling station (01508505). An alternate sampling station (01408508) was established 1.9 km downstream to collect the peak sample.

A continuous water-quality monitor (sonde) was deployed at each surface-water-quality sampling station to collect continuous water-quality data for the duration of the sampling events. The continuous monitors were used to measure and record water temperature, pH, specific conductance, dissolved-oxygen concentration, and turbidity at 5-minute intervals. All measurements were made continuously at each sampling station during base flow and stormflow, with the exception of Mill Creek; the sonde deployed at Mill Creek during the March sampling event was not equipped with a sensor to measure turbidity, so continuous turbidity measurements are not available for this storm event for Mill Creek.

Continuous water-quality monitors were deployed at the time of base-flow sample collection—prior to the onset of precipitation. Monitors were chained to bridge railings, tree trunks, or other secure objects and submerged at or near the bottom of each stream. Continuous monitors remained in the streams to collect data until stormflow-sample collection was complete. After the continuous monitors were retrieved, recorded data were uploaded to the USGS NWIS database. The continuous water-quality monitors were calibrated, operated, and maintained in accordance with procedures and requirements specified by Wagner and others (2006).

Calibration of all sonde sensors was performed prior to, and at the end of, each sampling event according to the manufacturer's recommendations and USGS standard protocols. Three pH standards (4, 7, and 10), three specific conductance standards (0, 180, and 500 microsiemens per centimeter (µS/cm)), and three turbidity standards (0, 50, and 100 Nephelometric Turbidity Units (NTU)) were used to check sensor calibration and make adjustments if necessary. The dissolved-oxygen sensors were calibrated to 100-percent O_2 saturation by using water-saturated laboratory air. The temperature sensors were checked by comparing readings with those of a certified laboratory thermometer. Analytical precision and reporting levels of the sensors are shown in table 4.

Groundwater

Groundwater samples were collected from five wells located within the BB-LEH watershed and screened in the Kirkwood-Cohansey aquifer system (fig. 4). Each well was sampled once during September 2010–May 2011, yielding a total of five environmental samples for the groundwater portion of the study. Four of the wells are located in an area that contributes direct groundwater discharge to the estuary, adjacent coastal wetlands, or minor coastal tributaries (Hunchak-Kariouk and Nicholson, 2001). One well (292097) is located in an area in which groundwater discharges to a stream—Long Swamp Creek—which flows into Toms River, and subsequently into the estuary. Two wells—291277 (53 meters (m) deep) and 292097 (24 m deep)— are domestic wells located in the northern portion of the watershed in highly urbanized areas near Toms River, New Jersey, although there are pockets of farmland in the immediate vicinity (less than 200 m) of well 291277. Well 290799 (17 m deep) is a municipal supply well located in a moderately developed area of Berkeley Township. Well 290743 (18 m deep) is a domestic well in a moderately developed area of Ocean Township. Well 291256 (21 m deep) is a domestic well in a sparsely developed area of Little Egg Harbor Township. Temperature, pH, specific conductance, dissolved-oxygen concentration, and turbidity were monitored while each well was pumped until measurements of all parameters were stable before samples were collected.

Table 4. Analytical precision of sensors used in a continuous water-quality monitor (sonde) for groundwater and surface-water sampling at stations in the Barnegat Bay-Little Egg Harbor watershed, 2010–11.

[˚C, degrees Celsius; mm Hg, millimeters of mercury; mg/L, milligrams per liter; NTU, nephelometric turbidity units; µS/cm, microsiemens per centimeter at 25˚C; --, not applicable]

Measurement (units of measurement)	Range	Resolution	Minimum reporting level
Air temperature (˚C)	-5 – 60	0.01	-5
Water temperature (˚C)	-5 – 60	0.01	-5
Barometric pressure (mm Hg)	500 – 800	0.1	500
Dissolved oxygen (mg/L)	0 – 50	0.01	0.0
Turbidity (NTU)	0 – 100	0.1	0.0
Specific conductance (µS/cm)	0 – 1,000	1.0	0.0
pH (standard units)	0 – 14	0.01	--

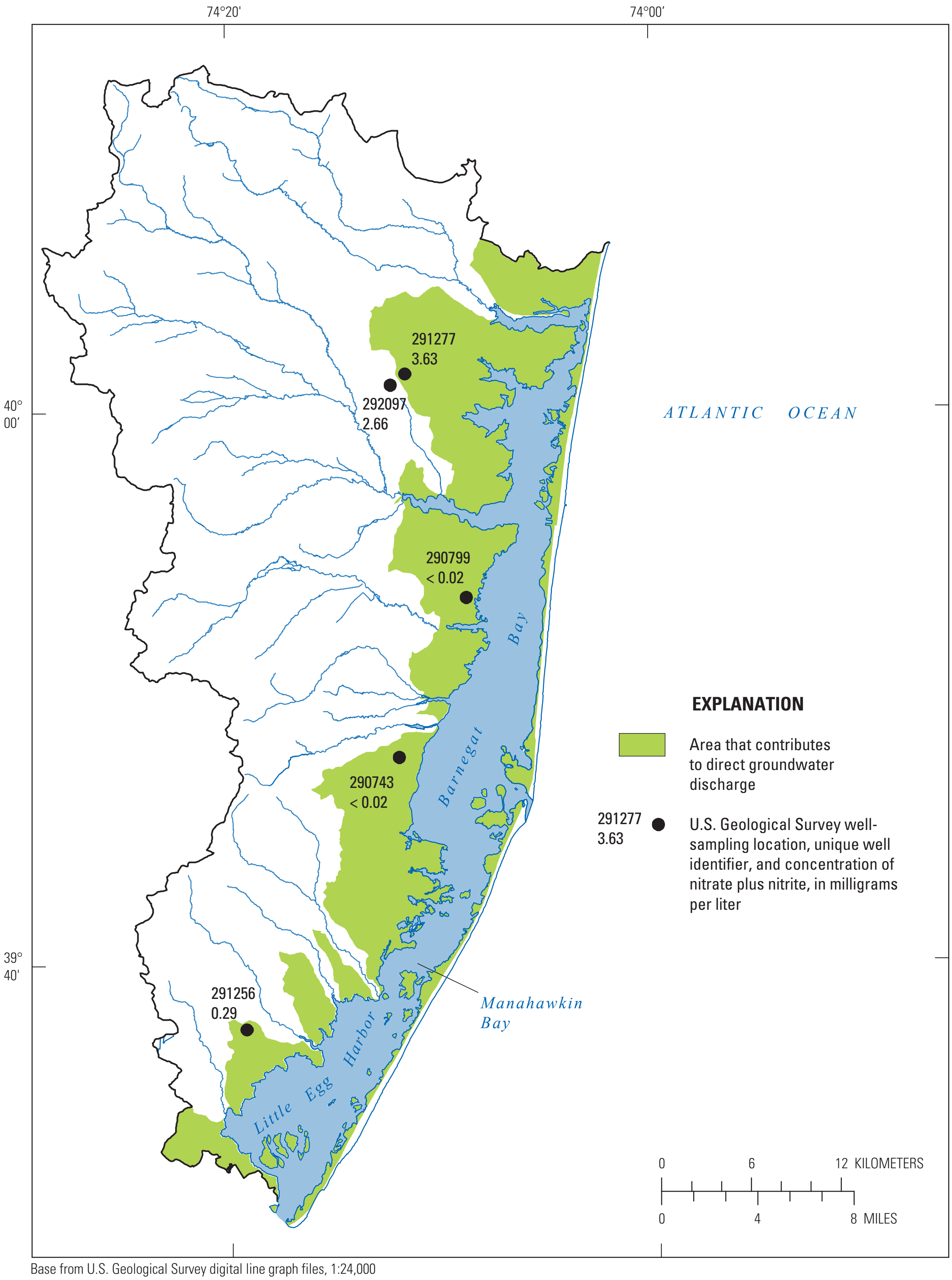

Figure 4. Locations of, and concentrations of nitrate plus nitrite in, five wells sampled within the Barnegat Bay-Little Egg Harbor watershed, 2010–11.

Quality Assurance and Quality Control

Quality assurance was achieved by following protocols as described in the National Field Manual (U.S. Geological Survey, 2006). Quality-control samples—field blanks and replicates—were collected at a rate of 20 percent of the number of environmental samples over the course of the study, such that five fields blanks and two sets of replicate samples were collected. Field blanks are used to measure the magnitude of contamination that may have been introduced during the collection, processing, shipping, or handling of samples, whereas replicate samples are used to characterize the amount of variability associated with sample collection.

Concentrations of water-quality constituents in five field blanks were compared to concentrations in corresponding environmental samples; two field blanks were collected during each of the two storm events, and one was collected at well 292097. Concentrations of compounds in the field blanks were either not detected or acceptable at concentrations less than three times those in the corresponding environmental sample, with one exception. The concentration of ammonia in the environmental sample collected at well 292097 (0.012 (mg/L) was less than the concentration in the corresponding field blank (0.017 mg/L); however, both concentrations are below the minimum reporting level for this constituent (0.02 mg/L) and are considered estimated values.

Two sets of replicate samples were collected at Toms River during the first storm event. The first set of replicates—collected during base flow—had higher concentrations of nitrogen (0.84 and 0.83 mg/L total nitrogen) and low variability. The second set of replicates—collected during peak flow—had lower concentrations (0.53 and 0.47 mg/L total nitrogen) and higher variability. This variability may be attributed to the high turbidity and suspended solids associated with the flood waters. To account for this variability, the average values for each set of replicate samples were used in the analysis for this report.

Water Quality Under Various Conditions in Surface Water and Groundwater

Surface Water

Continuous Water-Quality Data

Summary statistics of all continuous water-quality monitoring data are presented in appendix 1. Hydrographs showing changes in values of selected water-quality characteristics over the course of the sampling events are shown in figures 5 and 6. The range of values for each characteristic was normalized to a scale of 0 to 1 for graphical comparison.

Temperature

Water temperature in all five streams was dependent on season more than streamflow or whether the flow was dominated by base flow or stormflow. Prior to the nongrowing-season storm, mean base-flow temperatures ranged from 9.1 degrees Celsius (°C) (Cedar Creek) to 10.7 °C (Westecunk Creek). Over the course of the nongrowing-season storm, the mean water temperature at each site declined 1.3 to 2.3°C with the addition of colder rain water. Mean base-flow temperatures were substantially higher prior to the growing-season storm event, ranging from 16.2°C (Mill Creek) to 19.5°C (Toms River). Over the course of the growing-season storm, the mean temperature remained unchanged (Toms River), declined by about 0.1°C (Cedar Creek), or increased less than 1.5 °C (Mill Creek, Westecunk Creek, and North Branch Metedeconk River). Data from these two sampling events show that water temperature in streams in the Barnegat Bay-Little Egg Harbor (BB-LEH) watershed is relatively uniform among streams, is not greatly affected by precipitation, and is seasonally controlled such that temperatures are higher during and following the summer warm-up. Real-time temperature data collected over the 2010 water year for four of the five streams confirm the seasonal variability of, and the minor influence of precipitation events on, water temperature, which can in turn, affect instream biotic and abiotic reaction rates.

Specific Conductance

Specific conductance (SC) varied among the five streams. Prior to the major nongrowing-season storm, mean base-flow SC values were higher at the North Branch Metedeconk River (236 microsiemens per centimeter (µS/cm)) and Toms River (107 µS/cm) stations, and lower at the Cedar Creek (60 µS/cm), Mill Creek (89 µS/cm), and Westecunk Creek (36 µS/cm) stations. A similar pattern was present in mean base-flow SC values prior to the minor growing-season event, with values being highest in the North Branch Metedeconk River (216 µS/cm), intermediate in the Toms River (136 µS/cm), and lowest in the three southern streams (Cedar Creek, 44 µS/cm; Mill Creek, 79 µS/cm; and Westecunk Creek, 46 µS/cm). Higher concentrations of dissolved solids in the two northernmost streams are consistent with higher levels of urbanization, road salt and fertilizer applications, and atmospheric deposition being potential contributors. Mean SC values are lowest in the two least developed subbasins—Cedar Creek and Westecunk Creek—large areas of which are in the Pinelands Area. Extremely low dissolved-solids and low nutrient levels naturally characterize streams in the Pinelands.

SC decreased in the North Branch Metedeconk and Toms Rivers during the major nongrowing-season storm as large quantities of rainwater diluted the higher concentrations of dissolved solids found in base-flow water (fig. 5A–B). During the minor growing-season storm, SC in the North Branch Metedeconk and Toms Rivers decreased similarly with increasing streamflow, and then increased as streamflow attenuated (fig. 6A–B). SC in Cedar, Westecunk, and

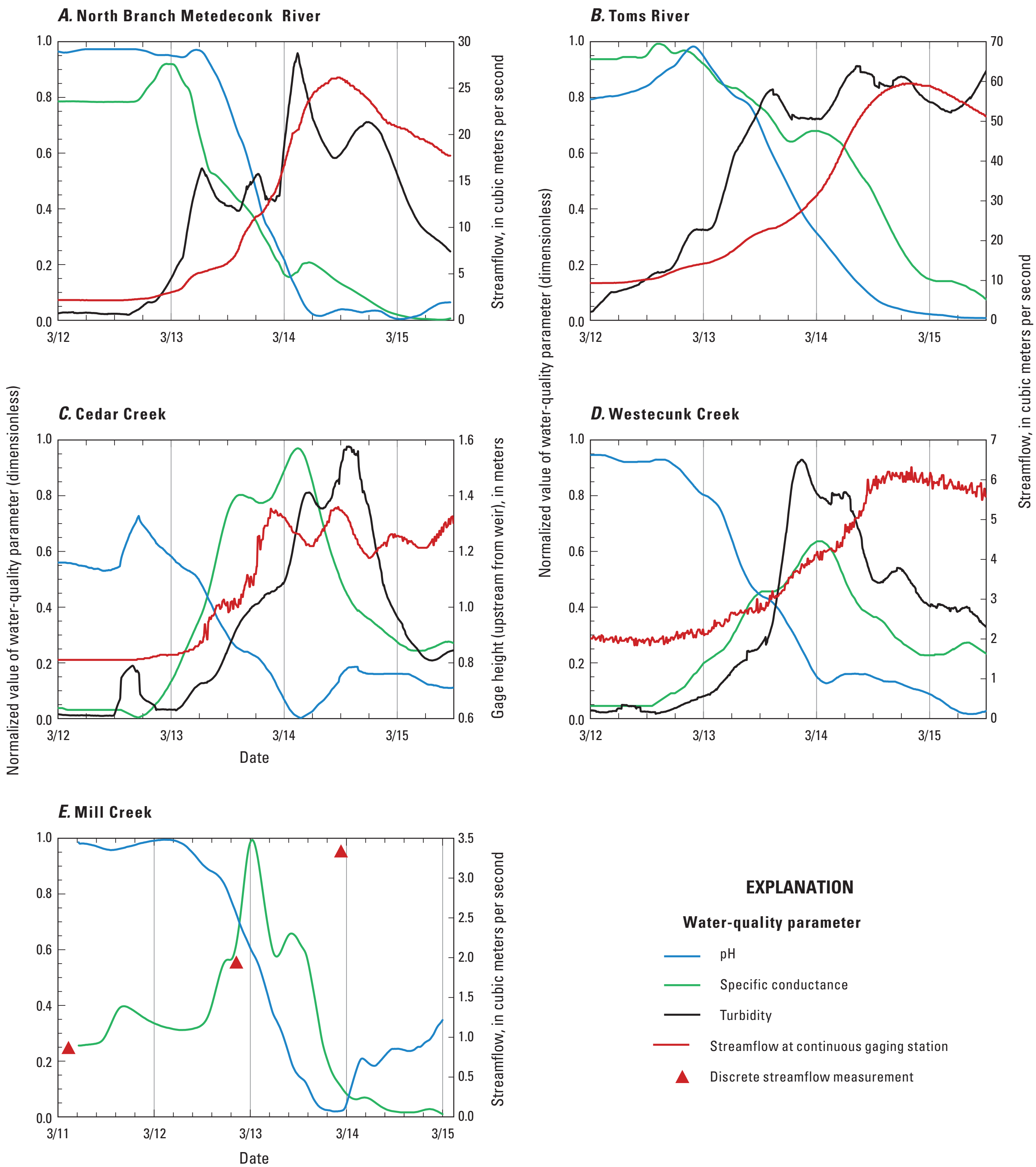

Figure 5. Hydrographs showing continuous water-quality-monitoring data recorded at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed during the nongrowing-season sampling event, March 2010. (The range of values for each water-quality parameter was normalized to a scale of 0 to 1 for graphical comparison.)

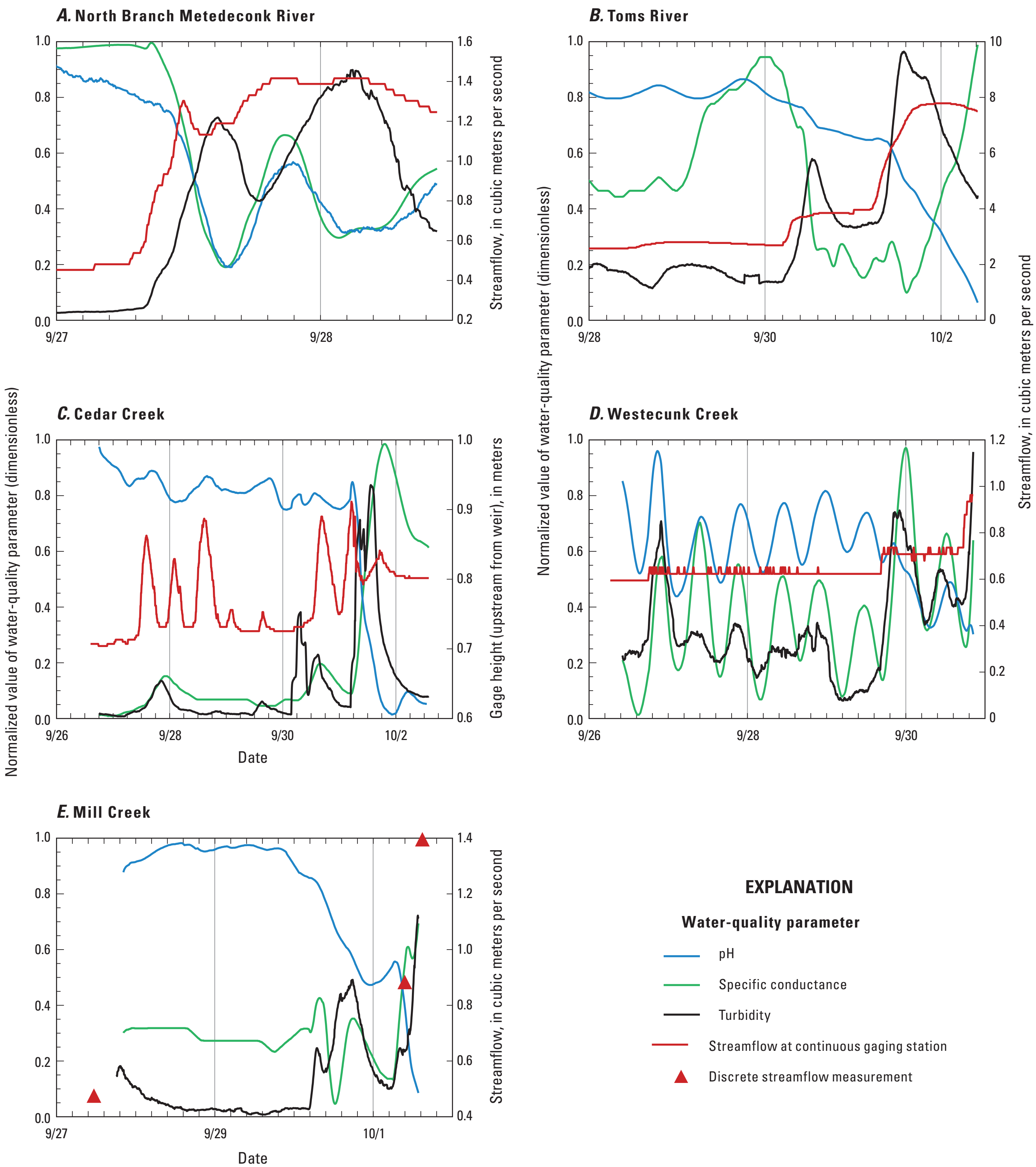

Figure 6. Hydrographs showing continuous water-quality-monitoring data recorded at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed during the growing-season sampling event, September–October 2010. (The range of values for each water-quality parameter was normalized to a scale of 0 to 1 for graphical comparison.)

Mill Creeks increased as streamflow increased during the major nongrowing-season storm (fig. 5C–E), as very low concentrations of dissolved solids in base-flow water were increased by the addition of dissolved solids carried in storm runoff. This pattern also occurred in Cedar and Mill Creeks during the minor growing-season storm (fig. 6C, E). The tidal control of SC during the smaller storm at Westecunk Creek masked any pattern of SC relative to streamflow (fig. 6D). These results indicate that dissolved solids in storm runoff were sufficiently concentrated to increase SC in the streams of the relatively undeveloped southern subbasins, whereas dilution by rainwater was sufficient to reduce SC in the northern, more developed subbasins to concentrations lower than those in base flow.

pH

The pH varied by site, by streamflow, and by season. The highest pH values were measured in the North Branch Metedeconk River, where mean values were consistently greater than or equal to 6.10. Cedar Creek, which is fed by groundwater and runoff from the highly acidic Pinelands environment, exhibited the lowest pH values; mean values were consistently less than 4.60 and were lowest (3.98) during the nongrowing-season event. The pH values at Mill Creek were slightly higher than those at the other two southern streams, possibly because of a higher percentage of urbanized land in the Mill Creek subbasin. Values of pH were greater during base flow than during stormflow at all sites for both storm events (fig. 5, 6), likely a result of dilution brought on by storm runoff and weak buffering capacity, as evidenced by low alkalinity values. The pH values varied by season, such that mean pH values were greater during the growing-season event than during the nongrowing-season event for all sites. Increased biological activity during the growing season results in the removal of carbon dioxide through photosynthesis, which shifts the carbonate equilibrium and raises the pH. Toms River showed the greatest difference in mean pH values among sampling events. During the nongrowing-season event, mean base-flow and stormflow values were 5.17 and 4.62, respectively; during the growing-season event, they were 6.39 and 6.19, respectively. The diluting effect of the large volume of rainwater during the substantial nongrowing-season event overwhelmed the buffering capacity of this stream, causing a decrease in pH to acidic levels.

The pattern of pH variability during storms closely resembles that of SC for the North Branch Metedeconk and Toms Rivers, except that pH in the Toms River continued to decline late in the minor growing-season storm, whereas SC increased (fig. 6B). Values of pH decreased with increasing streamflow in Cedar, Westecunk, and Mill Creeks during the major storm (fig. 5C–E) and at Cedar and Mill Creeks during the minor storm (fig. 6C, E). The variability in pH during tide cycling at Westecunk Creek masked any pH trend attributable to the storm event at this site (fig. 6D).

Dissolved Oxygen

Dissolved oxygen (DO) was at or near saturation values at all sites during base flow and stormflow. Mean DO concentrations in base flow ranged from 9.71 milligrams per liter (mg/L) (Mill Creek) to 10.60 mg/L (Toms River) prior to the nongrowing-season storm, and from 7.83 mg/L (Westecunk Creek) to 9.56 mg/L (Cedar Creek) prior to the growing-season storm. Mean DO concentrations for both base- and stormflow were 1 to 3 mg/L higher during the nongrowing-season sampling event than during the growing-season event at each site. This seasonal difference in DO concentration is attributable to higher saturation concentrations in colder water. DO is not a limiting factor for biological processes in these streams, nor does it appear to be substantially reduced or augmented by instream processes during either the minor growing-season or major nongrowing-season events, or during base flow in either season. This observation does not preclude the possibility of reduced DO concentrations in one or more of these streams in upstream reaches, or during extreme low-flow conditions.

Turbidity

Prior to the nongrowing-season event, mean turbidity values were highest at the North Branch Metedeconk River station (4.1 Nephelometric Turbidity Units (NTU)) and lowest at the Westecunk Creek station (0.5 NTU). Streamflow at the North Branch Metedeconk River station was about 2.15 cubic meters per second (m^3/s) during the nongrowing-season base-flow sample collection, which is substantially higher than typical base flow at this station (0.57–1.4 m^3/s), and likely contributed to the higher turbidity readings at this site. Flow was still receding from a major precipitation event that occurred during February 23–26, 2010. Prior to the growing-season storm event, mean turbidity values during base flow were less than 2.0 NTU at all sites, ranging from 1.8 NTU at the Toms River station to 0.8 NTU at the Cedar Creek station. Water levels at this time were lower than seasonal averages because drought conditions had persisted through much of the preceding summer. Flow was entirely from base flow, and in-stream turbulence was low. Therefore, the turbidity of streamwater was expected to be low. With the exception of Mill Creek, for which no data were collected during the nongrowing season, turbidity increased over the course of the storm at all stations during both the nongrowing- and growing-season events, as is evident in figures 5 and 6. Mean turbidity values increased most during stormflow at the North Branch Metedeconk River station (8–10 NTU) and least at the Westecunk Creek station (0.5–2.0 NTU), coincident with the degree of development in these subbasins. Mean turbidity values for stormflow were higher during the major storm event than during the minor event. The two least developed subbasins (Cedar Creek and Westecunk Creek) yielded storm runoff with the lowest mean turbidity readings.

Turbidity increased during both storms at all sites and declined after the streamflow had peaked (figs. 5 and 6). This result is important for nutrient loading to the BB-LEH estuary, as suspended-sediment transport occurs principally during storm events, and some of the nitrogen and most of the phosphorus is sediment-bound. Other consequences of substantial sediment loads to the estuary include light attenuation, which inhibits growth of aquatic plants, and sediment deposition on the estuary floor, which can reduce DO availability as well as bury benthic species to depths at which they cannot survive.

Turbidity values have been used to estimate concentrations of total suspended solids (TSS). Gao and others (2008) studied the relation between TSS and turbidity in an irrigation-dominated watershed in southeastern California. They found that linear functions can be used to relate concentration of TSS (mg/L) to turbidity (NTU) for high turbidity values, but overpredict TSS for turbidity values less than 30 NTU. They determined that a power function can be used to accurately estimate TSS values from a wider range of NTU values. Their best-fit model was

$$C = 3.6T^{0.8} \quad , \qquad (2)$$

where

$C = TSS$ (mg/L) and T = turbidity (NTU).

Relations between TSS and turbidity are site-specific. To accurately develop and use models to predict TSS from turbidity, data must be collected during varying flow conditions over a period of time that includes seasonal variability. TSS and turbidity data from 70 samples collected from streams in the BB-LEH watershed under various flow conditions were reviewed to determine whether a significant relation is evident. A power function of

$$C = 2.1T^{0.5} \qquad (3)$$

is described by the data; however, there is much uncertainty in the relation (r^2=0.4). Although the relation is not reliable for estimating TSS from turbidity in the BB-LEH watershed, the additional data show that the TSS for the streams sampled ranges from about 0 to 20 mg/L, and the turbidity range is about 0 to 20 NTU. Additional sampling for TSS analysis, especially early in precipitation events, would be needed to fully characterize the range of TSS in streams in this watershed. This information would be of value because excessive sediment has an adverse effect on the benthic community of the estuary, and because phosphorus, which can be the limiting nutrient of primary biological production when nitrogen is plentiful, is transported in surface water primarily as a particulate sorbate.

Nitrogen

Total Nitrogen

Total nitrogen in natural waters consists primarily of nitrite, nitrate, ammonia, and organic nitrogen. Concentrations of nitrogen species in water samples from the five streams studied are shown in table 5 and in figures 7 and 8. Base-flow total nitrogen concentrations at the North Branch Metedeconk River station were 1.32 and 1.25 mg/L for the nongrowing- and growing-season sampling events, respectively. Total nitrogen concentrations decreased to 0.59 and 0.85 mg/L during the nongrowing- and growing-season storm events, respectively. In this watershed, total nitrogen concentrations are lower in storm runoff than in base flow as a result of dilution by precipitation. Total nitrogen concentrations are substantially higher under all flow conditions and seasons in the North Branch Metedeconk subbasin than they are in the less developed, southern subbasins (Cedar, Mill, and Westecunk Creeks).

The concentration of total nitrogen in samples collected during base flow at the Toms River sampling station was considerably lower prior to the nongrowing-season event ([2]0.84 mg/L) than the growing-season event (1.36 mg/L). The large watershed provides substantial surface-water storage, resulting in a slow recession of stream discharge to base-flow conditions following precipitation events. The nongrowing-season sample was likely lower in total nitrogen than the growing-season sample because it was diluted by precipitation from recent storms, whereas the growing-season event occurred after a protracted dry period, and all base-flow streamwater was derived from groundwater discharge with little, if any, dilution from recent precipitation. Total nitrogen concentrations initially increased during the first flush of the nongrowing-season storm, mostly as a result of increases in organic nitrogen. Total nitrogen decreased during both storms, again most likely as a result of dilution from precipitation.

Total nitrogen concentrations in base-flow samples from Cedar Creek were 0.23 and 0.26 mg/L for the nongrowing- and growing-season sampling events, respectively. Nitrogen contributions from groundwater in this mostly undeveloped watershed appear to be low all year. Storm-flow concentrations were variable with season and over the course of the storm events but generally were lower than concentrations in more developed basins. The highest total nitrogen concentration at this site (0.57 mg/L) was measured during the first flush of the nongrowing-season event; the concentration declined to 0.25 mg/L at peak flow as additional rainwater diluted the nitrogen. For the growing-season event, concentrations increased to 0.39 mg/L at peak flow from nitrogen transported from the watershed in storm runoff, as the amount of precipitation was insufficient to provide a dilution effect.

Mill Creek samples had lower total nitrogen concentrations than samples from streams in either of the highly developed North Branch Metedeconk and Toms River subbasins but higher than those from streams in the mostly undeveloped Cedar and Westecunk Creek subbasins. The Mill Creek watershed is moderately (23 percent) developed and contains a large municipal landfill, which has been shown to contribute

[2] Replicate samples were collected at the Toms River station during the first sampling event. The average values for each set of replicate samples were used in the analysis.

Table 5. Concentrations of nutrient species in samples collected from five streams in the Barnegat Bay-Little Egg Harbor watershed, 2010.

[NG, nongrowing; G, growing; N, nitrogen; P, phosphorus; <, less than; BF, base flow; FF, first flush; PF, peak flow; constituent concentrations in milligrams per liter]

U.S. Geological Survey station number	Event number	Season	Date and time	Flow condition	Total N[1]	Nitrate plus nitrite	Ammonia plus organic N	Ammonia	Organic N[2]	Total P	Ortho-phosphate
01408120	1	NG	03/11/10 10:30	BF	1.32	1.05	0.27	0.027	0.24	0.02	0.008
01408120	1	NG	03/13/10 09:30	FF	0.88	0.56	0.32	0.026	0.29	0.06	0.009
01408120	1	NG	03/14/10 17:00	PF	0.59	0.27	0.32	< 0.010	0.32	0.04	0.011
01408120	2	G	09/26/10 10:20	BF	1.25	1.05	0.20	0.010	0.19	0.02	0.010
01408120	2	G	09/27/10 12:30	FF	0.90	0.65	0.25	0.122	0.13	0.09	0.009
01408120	2	G	09/28/10 10:15	PF	0.85	0.62	0.23	< 0.010	0.23	0.04	0.009
01408505	1	NG	[3]03/11/10 12:30	BF	0.83	0.49	0.34	0.088	0.25	< 0.01	< 0.004
01408505	1	NG	[3]03/11/10 12:30	BF	0.84	0.49	0.35	0.090	0.26	0.01	< 0.004
01408505	1	NG	03/13/10 11:55	FF	1.13	0.43	0.70	0.132	0.57	0.02	< 0.004
[4]01408508	1	NG	[3]03/15/10 13:45	PF	0.54	0.14	0.40	0.016	0.38	0.02	0.004
[4]01408508	1	NG	[3]03/15/10 13:45	PF	0.47	0.16	0.31	0.013	0.30	0.02	< 0.004
01408505	2	G	09/26/10 12:30	BF	1.36	1.16	0.20	0.057	0.14	< 0.01	0.006
01408505	2	G	09/28/10 12:10	FF	1.28	1.08	0.20	0.074	0.13	0.02	0.004
01408505	2	G	09/30/10 16:25	PF	1.05	0.80	0.25	0.081	0.17	0.03	0.004
01408950	1	NG	03/11/10 14:30	BF	0.23	0.06	0.17	< 0.010	0.17	< 0.01	< 0.004
01408950	1	NG	03/13/10 14:10	FF	0.57	0.09	0.48	< 0.010	0.48	< 0.01	< 0.004
01408950	1	NG	03/14/10 10:50	PF	0.25	0.05	0.20	< 0.010	0.20	< 0.01	< 0.004
01408950	2	G	09/26/10 15:35	BF	0.26	0.09	0.17	0.035	0.14	0.01	0.005
01408950	2	G	09/27/10 14:10	FF	0.17	0.09	0.08	0.039	0.04	< 0.01	0.005
01408950	2	G	10/01/10 12:00	PF	0.39	0.11	0.28	0.033	0.25	0.04	0.007
01409150	1	NG	03/11/10 12:30	BF	0.43	0.10	0.33	0.227	0.10	< 0.01	0.004
01409150	1	NG	03/13/10 11:30	FF	0.46	0.17	0.29	0.062	0.23	< 0.01	< 0.004
01409150	1	NG	03/14/10 18:50	PF	0.27	0.06	0.21	0.054	0.16	< 0.01	< 0.004
01409150	2	G	09/27/10 11:10	BF	0.62	0.12	0.50	0.417	0.08	< 0.01	0.005
01409150	2	G	10/01/10 10:00	FF	0.65	0.07	0.58	0.205	0.38	< 0.01	< 0.004
01409150	2	G	10/01/10 13:45	PF	0.65	0.03	0.62	0.132	0.49	0.01	< 0.004

Table 5. Concentrations of nutrient species in samples collected from five streams in the Barnegat Bay-Little Egg Harbor watershed, 2010.—Continued

[NG, nongrowing; G, growing; N, nitrogen; P, phosphorus; <, less than; BF, base flow; FF, first flush; PF, peak flow; constituent concentrations in milligrams per liter]

U.S. Geological Survey station number	Event number	Season	Date and time	Flow condition	Total N[1]	Nitrate plus nitrite	Ammonia plus organic N	Ammonia	Organic N[2]	Total P	Ortho-phosphate
01409281	1	NG	03/11/10 10:30	BF	0.17	0.05	0.12	< 0.010	0.12	< 0.01	0.004
01409281	1	NG	03/13/10 09:20	FF	0.25	0.06	0.19	< 0.010	0.19	< 0.01	< 0.004
01409281	1	NG	03/14/10 13:15	PF	0.20	0.03	0.17	< 0.010	0.17	< 0.01	< 0.004
01409281	2	G	09/26/10 17:55	BF	0.16	0.06	0.10	0.013	0.09	< 0.01	0.006
01409281	2	G	10/01/10 08:30	FF	0.27	0.07	0.20	0.020	0.18	< 0.01	0.006
01409281	2	G	10/01/10 12:50	PF	0.30	0.08	0.22	0.018	0.20	0.01	0.006

[1]Concentrations of total nitrogen were calculated as the sum of nitrate plus nitrite and ammonia plus organic nitrogen.

[2]Concentrations of organic nitrogen were calculated by subtracting the value for ammonia from the value for ammonia plus organic nitrogen. In cases where the ammonia concentration was less than the minimum detection level (MDL), one-half of the MDL for ammonia was used in the calculation.

[3]Replicate sample collected.

[4]As a result of overbank flooding, peak-flow sample collection on the Toms River was conducted at station number 01408508 for storm event 1.

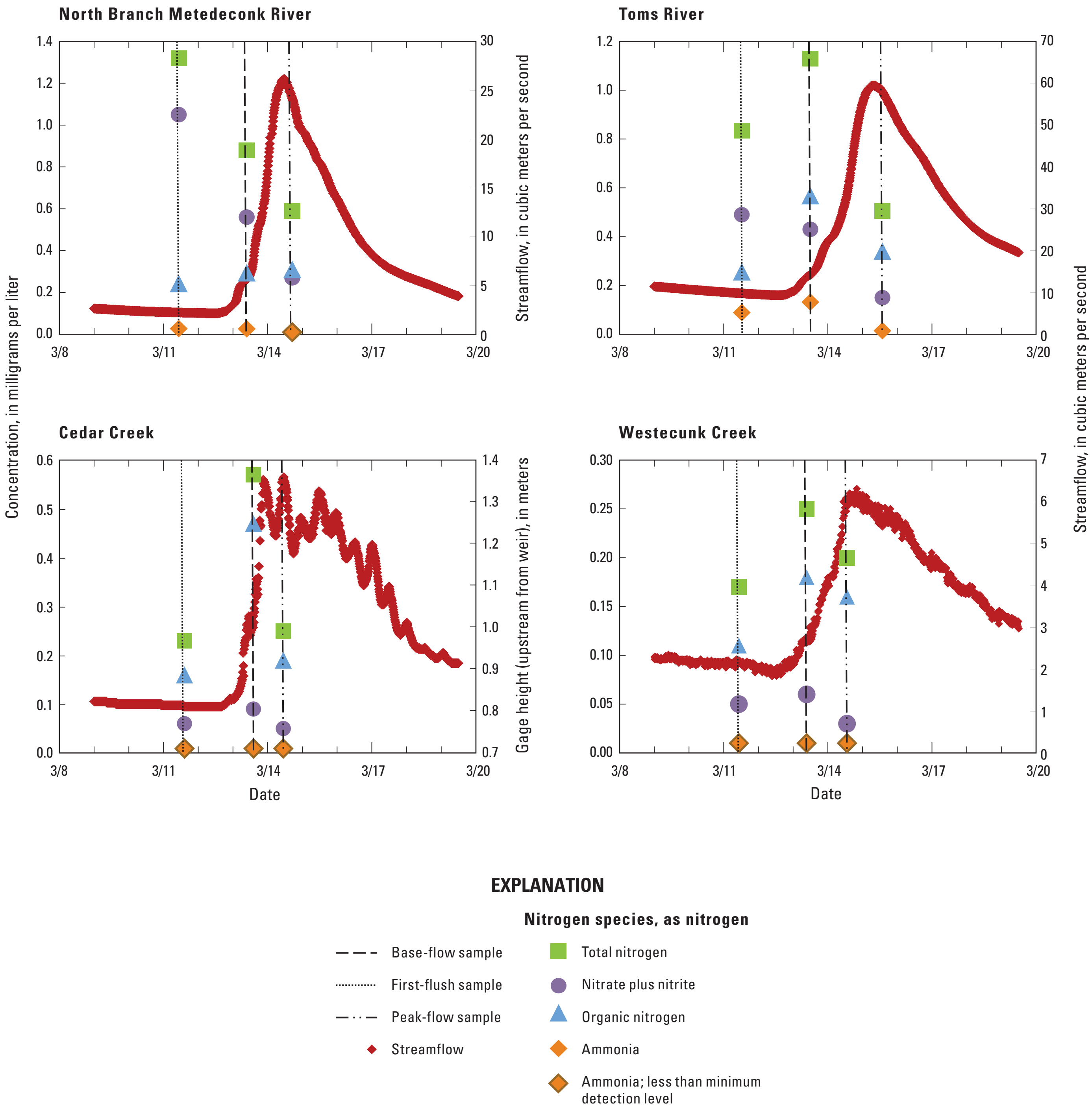

Figure 7. Streamflow hydrographs and concentrations of total nitrogen, nitrate plus nitrite, organic nitrogen, and ammonia in surface-water samples collected at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed during the nongrowing-season sampling event, March 2010. (For Toms River, the average of the replicate values (for base flow and peak flow) was plotted for all constituents.)

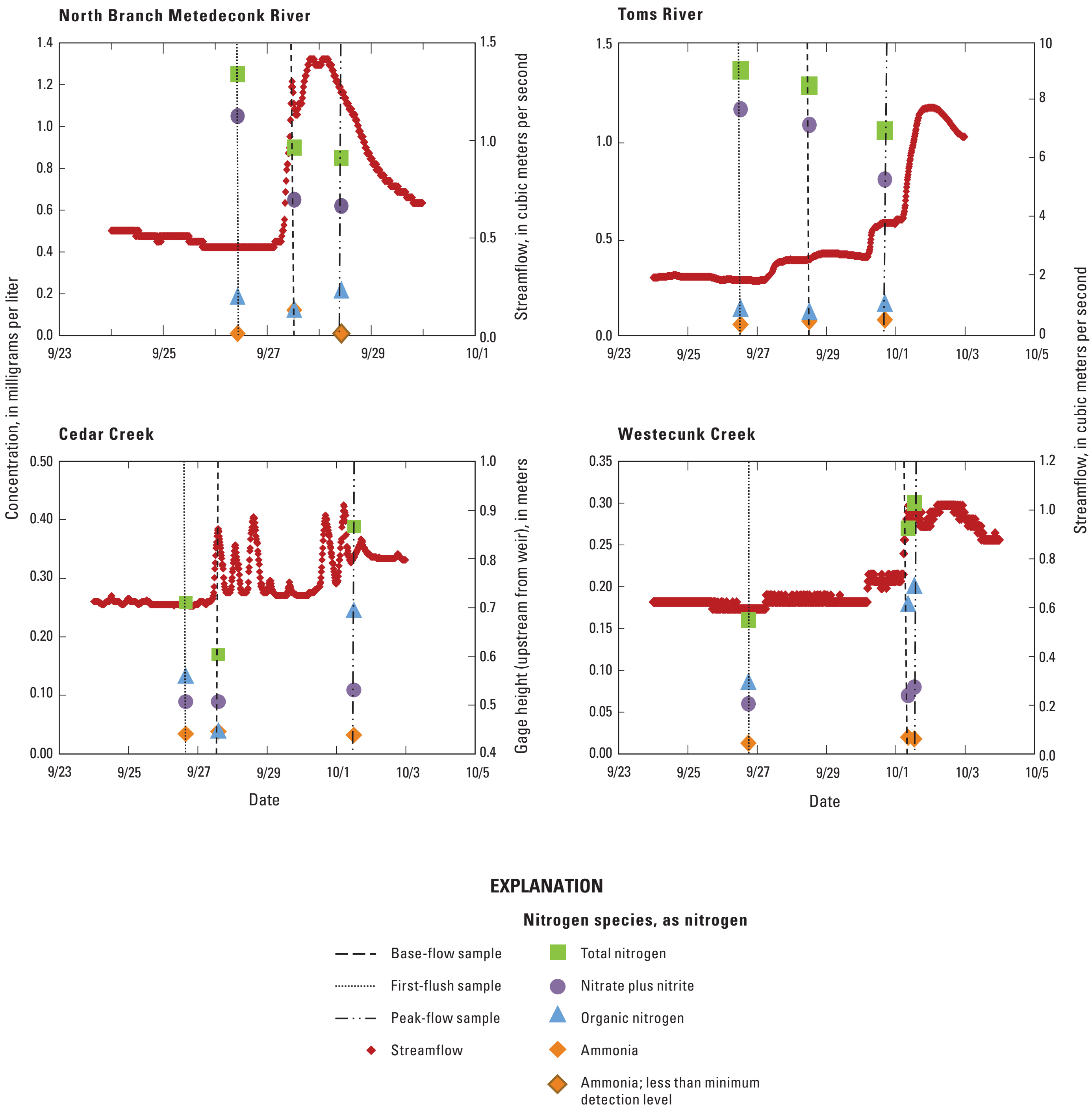

Figure 8. Streamflow hydrographs and concentrations of total nitrogen, nitrate plus nitrite, organic nitrogen, and ammonia in surface-water samples collected at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed during the growing-season sampling event, September–October 2010.

nitrogen to the groundwater and to Mill Creek (New Jersey Pinelands Commission, 2006a). Base-flow concentrations were 0.43 mg/L (nongrowing season) and 0.62 mg/L (growing season). Stormflow concentrations were highest during the growing-season event (0.65 mg/L during first flush and peak flow). As with the North Branch Metedeconk River, Toms River, and Cedar Creek, large amounts of rainwater appear to dilute the total nitrogen concentrations during the major nongrowing-season storm but, in this case, not during the minor growing-season event.

Total nitrogen concentrations generally were lowest in Westecunk Creek, the southernmost stream sampled. The subbasin of this stream is lightly (less than 4 percent) developed. Base-flow concentrations were 0.17 and 0.16 mg/L for the nongrowing- and growing-season samples, respectively. Total nitrogen concentrations increased during both storms, and the highest value, 0.30 mg/L, occurred at peak flow during the growing-season event. The increase was mostly from organic nitrogen, probably from natural sources, which had accumulated on the land surface between storm events from decomposing plant and animal matter and was carried to the stream in runoff.

Historical total nitrogen data for 1980–2009 were retrieved from the USGS NWIS database for comparison with data collected during this investigation to determine whether nutrient concentrations in the limited number of samples collected are representative of historical data. In cases in which historical data for a site were not available in NWIS, data from the U.S. Environmental Protection Agency Storage and Retrieval (STORET) database were used. For this comparison, growing- and nongrowing-season data were pooled. Sample-collection sites varied somewhat from those previously used; therefore, some differences in concentrations were expected. The median total nitrogen concentration for each stream during base-flow and stormflow conditions is shown in table 6. There is relatively close agreement among current and historical median total nitrogen concentrations, particularly for Cedar, Mill, and Westecunk Creeks. However, median total nitrogen concentrations for the North Branch Metedeconk and Toms Rivers from the 2010 sampling effort are considerably higher than the historical concentrations. These higher concentrations are consistent with studies of water-quality trends, which indicate that concentrations of dissolved nitrate plus nitrite in both the Metedeconk and Toms River watersheds are increasing (Hickman and Barringer, 1999; Hickman and Gray, 2010).

These data indicate that total nitrogen concentrations in these five streams are related to the land use (current or historical) within the subbasin. The basins of the North Branch Metedeconk and Toms Rivers are the most developed subbasins, and these streams exhibit the highest concentrations of total nitrogen. The Mill Creek subbasin is moderately developed, and total nitrogen concentrations in the stream are moderate. Cedar Creek and Westecunk Creek have largely undeveloped subbasins and have the lowest total nitrogen values. Concentrations in these five streams during precipitation events tend to remain unchanged or increase from base-flow values early in the storm, but a diluting effect on total nitrogen concentrations later in the storm is observed during major events.

Nitrate plus Nitrite

Nitrite (NO_2^-) typically is absent or is present in small concentrations relative to nitrate (NO_3^-) in natural waters because it is a thermodynamically unstable intermediate in the microbially mediated nitrogen cycle; it is rapidly converted to nitrate in oxygenated water and is reduced to ammonia under anoxic conditions. Nitrite was either not detected (detection limit 0.001 mg/L) or was detected as less than 6 percent of the total of nitrate plus nitrite (more typically less than 1 percent) in samples collected for this investigation. Therefore, nitrite concentrations are not reported separately here, and for the purposes of this study, concentrations of nitrate plus nitrite can be considered to represent nitrate concentrations.

Nitrate is the most abundant nitrogen species in the North Branch Metedeconk River, especially during base flow (figs. 7, 8). The base-flow nitrate plus nitrite concentration prior to both storms was 1.05 mg/L, which represents approximately 80 percent of the total nitrogen mass during base flow. Nitrate plus nitrite concentrations decreased to 0.27 mg/L (46 percent of the total nitrogen) during the nongrowing-season storm and to 0.62 mg/L (73 percent of the total nitrogen) during the growing-season storm. The contribution of nitrate plus nitrite may have been lower during the nongrowing-season storm as a result of a reduced contribution from applied inorganic fertilizer or of greater dilution resulting from the major precipitation event.

The nitrate plus nitrite concentration in base flow at Toms River was 0.49 mg/L (59 percent of the total nitrogen) and 1.16 mg/L (85 percent of the total nitrogen) during the nongrowing and growing seasons, respectively. This large difference in base-flow nitrate plus nitrite concentration between seasons may be explained by the influence of dilution from recent recharge on the nongrowing-season sample, and (or) it may be the result of a reduced contribution from fertilizer application during the nongrowing season. As in the Metedeconk River Basin, nitrate plus nitrite is the dominant nitrogen species during base flow, and nitrate plus nitrite concentrations (and nitrate as a percentage of total nitrogen) decreased over the course of both storms. Nitrate plus nitrite accounted for less than 40 percent of the total nitrogen in stormflow samples during the nongrowing season and greater than 75 percent during the growing season.

Nitrate plus nitrite was not the predominant nitrogen contributor at streams in the three less developed, southern watersheds. Base-flow nitrate plus nitrite concentrations ranged from 0.05 mg/L (Westecunk Creek) to 0.12 mg/L (Mill Creek) and accounted for less than 40 percent of the total nitrogen concentration at each of these three sites. Base-flow concentrations were slightly higher at all three sites during the growing season than during the nongrowing season. Concentrations of nitrate plus nitrite increased or decreased variably

Table 6. Median nutrient concentrations for streams in the Barnegat Bay-Little Egg Harbor watershed measured in samples collected for this study (2010), and determined from historical water-quality data for 1980–2009.

[mg/L, milligrams per liter; NB, North Branch; --, not available; <, less than]

Stream	Flow condition	Median total nitrogen concentration, in mg/L (number of samples)		Median total phosphorus concentration, in mg/L (number of samples)	
		Current	Historical	Current	Historical
NB Metedeconk River	Base flow	1.29 (2)	0.89 (27)	0.02 (2)	0.04 (27)
NB Metedeconk River	Stormflow	0.87 (4)	0.76 (12)	0.05 (4)	0.05 (12)
Toms River	Base flow	1.10 (2)	0.83 (37)	< 0.01 (2)	0.02 (64)
Toms River	Stormflow	1.10 (4)	0.75 (26)	0.02 (4)	0.02 (43)
Cedar Creek	Base flow	0.25 (2)	< 0.17 (30)	< 0.01 (2)	< 0.01 (30)
Cedar Creek	Stormflow	0.32 (4)	< 0.24 (7)	< 0.01 (4)	< 0.01 (7)
Mill Creek	Base flow	0.53 (2)	--	< 0.01 (2)	0.02 (3)
Mill Creek	Stormflow	0.56 (4)	0.64 (3)	< 0.01 (4)	--
Westecunk Creek	Base flow	0.17 (2)	0.20 (11)	< 0.01 (2)	0.01 (11)
Westecunk Creek	Stormflow	0.26 (4)	0.26 (4)	< 0.01 (4)	< 0.02 (2)

over the course of the storms; stormflow concentrations ranged from less than 0.05 mg/L (Mill Creek during the growing season and Westecunk Creek during the nongrowing season) to 0.17 mg/L (Mill Creek during the nongrowing season) and accounted for less than 40 percent of the total nitrogen concentration in stormflow samples, except at Cedar Creek during the growing season, when it accounted for 53 percent.

Ammonia

Ammonia is present in trace amounts in all streams under most flow conditions, except Mill Creek, in which it accounts for, on average, 60 percent of the base-flow total nitrogen concentration. The base-flow concentration of ammonia was 0.227 mg/L during the nongrowing season and 0.417 mg/L during the growing season at Mill Creek but was less than 0.100 mg/L at all other streams during base flow. The concentration of ammonia (and ammonia as a percentage of total nitrogen) at Mill Creek decreased over the course of both storms, indicating dilution by storm runoff. An expansive domestic-waste landfill located upstream from the sampling point on Mill Creek has been associated with groundwater contamination, including high concentrations of ammonia (New Jersey Pinelands Commission, 2006a; New Jersey Pinelands Commission, 2006b). This is probably the point source of most of the ammonia in the Mill Creek samples. The Metedeconk and Toms Rivers both exhibited concentrations of ammonia greater than 0.100 mg/L during the first flush of one storm event.

Organic Nitrogen

In general, concentrations of organic nitrogen appear to be greater in the more developed than in the less developed subbasins; however, the ratio of organic nitrogen to total nitrogen is greater in the less developed subbasins. Although average base-flow concentrations of organic nitrogen are higher in the North Branch Metedeconk (0.22 mg/L) and Toms (0.20 mg/L) Rivers than in the other streams, the ratio of organic nitrogen to total nitrogen is much lower in base flow (less than 35 percent) than in the other streams sampled. Septic and sewage effluent and organic fertilizers are potential sources of organic nitrogen in developed areas that are less prevalent in undeveloped areas. For both the North Branch Metedeconk and Toms Rivers, concentrations of organic nitrogen in both base-flow and stormflow samples were higher during the nongrowing season than during the growing season, with nongrowing-season stormflow proportions reaching 54 and 67 percent at the Metedeconk and Toms River stations, respectively.

Organic nitrogen is the dominant species of nitrogen in nearly all samples collected from Cedar and Westecunk Creeks, and in all stormflow samples collected from Mill Creek (where nitrogen in base flow is dominated by ammonia). The average base-flow concentration of organic nitrogen, 0.16 mg/L at Cedar Creek and 0.11 mg/L at Westecunk Creek, accounted for more than 50 percent of the total nitrogen in base flow at these sites. Stormflow concentrations generally were greater than those in base flow and, in some cases, made up more than 75 percent of the total nitrogen in stormflow samples from Cedar, Mill, and Westecunk Creeks. The subbasins of these streams are the least developed, and more than 80 percent of their area lies within the Pinelands Area, indicating natural inputs of organic nitrogen to the streams that increase during periods of storm runoff.

Phosphorus

Total phosphorus and orthophosphate were either not detected or measured at very low concentrations in surface-water samples (table 5). North Branch Metedeconk River samples had the highest levels of total phosphorus (0.02–0.09 mg/L) and orthophosphate (0.008–0.011 mg/L). Total phosphorus was not detected at levels above 0.04 mg/L as P in samples from all other streams. Orthophosphate was detected at very low but measurable concentrations more frequently during the growing season sampling event. The absence of substantial concentrations of phosphorus in the samples collected indicates that the streams may be phosphorus-limited under some conditions.

Like total nitrogen data, historical phosphorus data for 1980 to 2009 (table 6) were retrieved from NWIS or from STORET when NWIS data were not available. Median phosphorus concentrations from the current study are in close agreement with historical data for all streams studied, with phosphorus either not detected or measured at very low concentrations. North Branch Metedeconk River is the only stream in which reportable concentrations of phosphorus were detected, either in samples collected for this study or in historic data.

Dissolved Solids

In general, concentrations of dissolved solids (including major ions such as chloride (Cl^-) and potassium (K^+)) in base flow were highest in samples collected at the North Branch Metedeconk River station (greater than 42 mg/L for Cl^- and greater than 2.3 mg/L for K^+), followed by the Toms River station (greater than 20 mg/L for Cl^- and greater than 1.2 mg/L for K^+). For the North Branch Metedeconk and Toms Rivers, concentrations of Cl^- and K^+ were highest during base flow and decreased during stormflow, indicating dilution by storm runoff. Higher values at North Branch Metedeconk River during the nongrowing-season sampling event than during the growing-season event, as well as an increase in Cl^- values at Toms River during the first flush of the nongrowing-season event, may be related to the application of road salt during winter months; however, the pattern of higher values of Cl^- and K^+ during base flow than during stormflow at North Branch Metedeconk River is not season-dependent and indicates the likelihood of a source other than road salt for the elevated dissolved-solids concentrations at this site.

Concentrations of dissolved solids in base flow were lowest in samples collected at the Cedar and Westecunk Creek stations (less than 11 mg/L for Cl^- and less than 0.6 mg/L for K^+). These streams have the least developed subbasins in the study area, and the natural characteristics of waters within these subbasins, including low concentrations of dissolved solids, remain relatively undisturbed. Although concentrations of Cl^- and K^+ at these two stations were consistently low (less than 15 mg/L) under all flow conditions, higher concentrations of Cl^- and K^+ tended to occur during stormflow, indicating an influx of dissolved solids with storm runoff.

Groundwater

Nitrogen

Concentrations of nitrogen species in water samples from the five wells (fig. 4) are shown in table 7. The two wells farthest north (291277 and 292097) have total nitrogen concentrations of 3.66 and 2.69 mg/L as nitrogen, respectively, 99 percent of which is in the form of nitrate. Total nitrogen concentrations in wells 290799 and 290743, both of which are located in moderately developed coastal areas, were less than 0.07 mg/L, with concentrations of nitrate plus nitrite not detected. The southernmost well (291256) had a total nitrogen concentration of 0.32 mg/L, with a nitrate plus nitrite concentration of 0.29 mg/L. Concentrations of ammonia plus organic nitrogen were less than the minimum detection level (MDL) for all samples (table 3).

Historical water-quality measurements made by using sampling and analytical conditions comparable to those used in the current study were available for two of these wells in the USGS NWIS database. Well 291277 was sampled previously in 1998 with a nitrate plus nitrite concentration of 1.77 mg/L and in 2006 with a nitrate plus nitrite concentration of 3.33 mg/L. With the most recent nitrate plus nitrite value of 3.63 mg/L, and all three samples having been collected under oxic conditions, nitrate concentrations at this site appear to be increasing; however, additional sample-analysis data would be helpful for confirming this apparent trend. Well 290743 was last sampled in 1982 and had a nitrate plus nitrite concentration of 0.13 mg/L. The concentration in the most recent sample was less than the MDL. Dissolved oxygen levels at wells 290743 and 290799 during this sampling event were extremely low (0.2–0.3 mg/L). The anoxic environment may have led to nitrate losses through denitrification, contributing to the nondetects in samples from these two wells.

Phosphorus

Total phosphorus was not found at detectable concentrations in any of the wells sampled. These results are to be expected because phosphorus tends to adsorb to sediments and typically is not found in the dissolved phase in groundwater. Orthophosphate was not detected in either of the two northernmost wells, which have the most heavily developed contributing areas. Extremely low concentrations (0.005–0.009 mg/L) were measured in the other three wells. Overall, phosphorus in

Table 7. Concentrations of nutrient species, and values of nitrogen and oxygen stable isotope ratios in nitrate, in samples collected from five wells screened in the Kirkwood-Cohansey aquifer system in the Barnegat Bay-Little Egg Harbor watershed, 2010–11.

[N, nitrogen; P, phosphorus; <, less than; --, not available; constituent concentrations in milligrams per liter]

U.S.Gelogical Survey station number	Date	Well depth, in meters	Water use	Total N[1]	Nitrate plus nitrite	Ammonia plus organic N	Total P	Ortho-phosphate	$\delta^{15}N$, in per mil	$\delta^{18}O$, in per mil
290743	09/01/2010	18	Domestic	< 0.07	< 0.02	< 0.05	< 0.01	0.009	--	--
290799	09/14/2010	17	Public supply	< 0.07	< 0.02	< 0.05	< 0.01	0.009	--	--
291256	09/22/2010	21	Domestic	0.32	0.29	< 0.05	< 0.01	0.005	6.00	4.07
291277	05/17/2011	53	Domestic	3.66	3.63	< 0.05	< 0.01	< 0.004	5.09	3.17
292097	04/28/2011	24	Domestic	2.69	2.66	< 0.05	< 0.01	< 0.004	4.12	2.07

[1]Concentrations of total nitrogen were calculated as the sum of nitrate plus nitrite and ammonia plus organic nitrogen. In cases where both constituent concentrations were less than the minimum detection limit (MDL), the concentration of total nitrogen is less than the sum of the MDLs. In cases where one constituent concentration was less than the MDL, one-half of the MDL for that constituent was used in the calculation. Total nitrogen values may differ from those reported in the National Water Information System database.

the groundwater represented by these five samples would not contribute substantially to the phosphorus concentrations and loads in surface water were this water to discharge to streams in the watershed.

Stable Isotope Analysis

Surface Water

Values of $\delta^{18}O$ and $\delta^{15}N$ for all surface-water samples collected (table 8, figure 9A) are indicative of mixing of nitrogen within the watershed from multiple sources. Many of the data points are clustered within the overlapping fields of nitrogen originating from soil and animal and septic waste; several points are just outside the common ranges for nitrogen from synthetic and ammonium fertilizers. None of the points fall within or near the typical range of $\delta^{18}O$ values for atmospheric nitrate, indicating that the atmosphere is not a predominant source of nitrogen in the streams sampled. Generally, $\delta^{18}O$ values were higher, and $\delta^{15}N$ values were lower, during stormflow than during base flow.

On a plot of the relation between $\delta^{18}O$ and $\delta^{15}N$ values for base-flow samples (fig. 9B), all points fall within the overlapping fields of nitrogen originating from soil and animal and septic waste, and just outside the common range for nitrogen from ammonium in fertilizer and precipitation. This observation indicates that a mixing of nitrogen from multiple subsurface sources carried in groundwater likely contributes to the base-flow nitrogen load. Over the two sampling events, $\delta^{15}N$ values ranged from +6.04 to +9.29 per mil (‰) during base flow; the highest base-flow $\delta^{15}N$ value for both sampling events was measured in a sample from Westecunk Creek. The $\delta^{15}N$ values ranged from +4.88 to +10.21 ‰ during stormflow (first flush and near peak). The wider range of values during stormflow indicates that mixing was slightly greater during stormflow than during base flow. There was an overall decrease in $\delta^{15}N$ values at all sites over the course of the nongrowing-season storm (fig. 10A) and at Cedar and Westecunk Creeks during the growing-season storm (fig. 10B). The lower $\delta^{15}N$ values indicate a greater influence of nitrogen that originated as atmospheric nitrate, as ammonium in fertilizer or precipitation, as synthetic nitrate fertilizer, or some combination thereof, and a smaller influence of nitrogen from animal and septic waste during stormflow than during base flow. The higher $\delta^{15}N$ isotopic signature at Westecunk Creek, coupled with the presence of a nearby wastewater-pumping facility and a sewage odor documented during sampling, is consistent with sewage effluent as a source of nitrogen input to this stream. However, the nitrate concentration within this subbasin was very low (less than 0.1 mg/L); therefore, any contribution from sewage is minimal.

Over the two sampling events, $\delta^{18}O$ values ranged from +1.03 to +10.85 ‰ during base flow and from +2.05 to +19.61 ‰ during stormflow (first flush and near peak), again indicating a greater mixing of sources during stormflow. Much of the variation in the $\delta^{18}O$ values during stormflow occurred during the first storm event, during which a substantial amount of precipitation fell on the watershed. There was an overall increase in $\delta^{18}O$ values at all sites over the course of the nongrowing-season storm (fig. 11A), and, to a lesser degree, at all sites except Mill Creek during the growing-season storm (fig. 11B). The higher $\delta^{18}O$ values during stormflow indicate a greater influence of nitrogen from the atmosphere during stormflow than during base flow.

In general, there was a shift from higher $\delta^{15}N$ and lower $\delta^{18}O$ values during base-flow conditions to lower $\delta^{15}N$ and higher $\delta^{18}O$ values as the storms progressed and flows increased. This pattern is shown in a plot of the average $\delta^{15}N$

Table 8. Values of nitrogen and oxygen stable isotope ratios in nitrate in samples collected from five streams in the Barnegat Bay-Little Egg Harbor watershed, 2010.

[NG, nongrowing; G, growing; BF, base flow; FF, first flush; PF, peak flow]

U.S. Gelogical Survey station number	Event number	Season	Date and time	Flow condition	$\delta^{15}N$, in per mil	$\delta^{18}O$, in per mil
01408120	1	NG	03/11/10 10:30	BF	6.91	3.65
01408120	1	NG	03/13/10 09:30	FF	5.98	8.86
01408120	1	NG	03/14/10 17:00	PF	4.98	6.70
01408120	2	G	09/26/10 10:20	BF	8.30	2.56
01408120	2	G	09/27/10 12:30	FF	7.06	5.96
01408120	2	G	09/28/10 10:15	PF	7.96	5.21
01408505	1	NG	[1]03/11/10 12:30	BF	6.90	3.36
01408505	1	NG	[1]03/11/10 12:30	BF	7.07	3.28
01408505	1	NG	03/13/10 11:55	FF	6.54	6.81
[2]01408508	1	NG	[1]03/15/10 13:45	PF	5.55	9.90
[2]01408508	1	NG	[1]03/15/10 13:45	PF	6.14	11.52
01408505	2	G	09/26/10 12:30	BF	6.04	1.03
01408505	2	G	09/28/10 12:10	FF	6.29	2.05
01408505	2	G	09/30/10 16:25	PF	6.41	2.22
01408950	1	NG	03/11/10 14:30	BF	7.19	5.86
01408950	1	NG	03/13/10 14:10	FF	6.63	17.88
01408950	1	NG	03/14/10 10:50	PF	5.93	16.95
01408950	2	G	09/26/10 15:35	BF	6.81	3.98
01408950	2	G	09/27/10 14:10	FF	6.74	9.81
01408950	2	G	10/01/10 12:00	PF	5.10	8.78
01409150	1	NG	03/11/10 12:30	BF	6.90	5.28
01409150	1	NG	03/13/10 11:30	FF	5.72	9.15
01409150	1	NG	03/14/10 18:50	PF	4.88	14.61
01409150	2	G	09/27/10 11:10	BF	7.05	10.85
01409150	2	G	10/01/10 10:00	FF	6.76	7.65
01409150	2	G	10/01/10 13:45	PF	6.76	9.02
01409281	1	NG	03/11/10 10:30	BF	9.29	9.49
01409281	1	NG	03/13/10 09:20	FF	10.21	19.61
01409281	1	NG	03/14/10 13:15	PF	5.40	16.42
01409281	2	G	09/26/10 17:55	BF	8.50	6.98
01409281	2	G	10/01/10 08:30	FF	7.38	8.65
01409281	2	G	10/01/10 12:50	PF	6.24	8.50

[1]Replicate sample collected.

[2]As a result of overbank flooding, peak-flow sample collection on the Toms River was conducted at station number 01408508 for storm event 1.

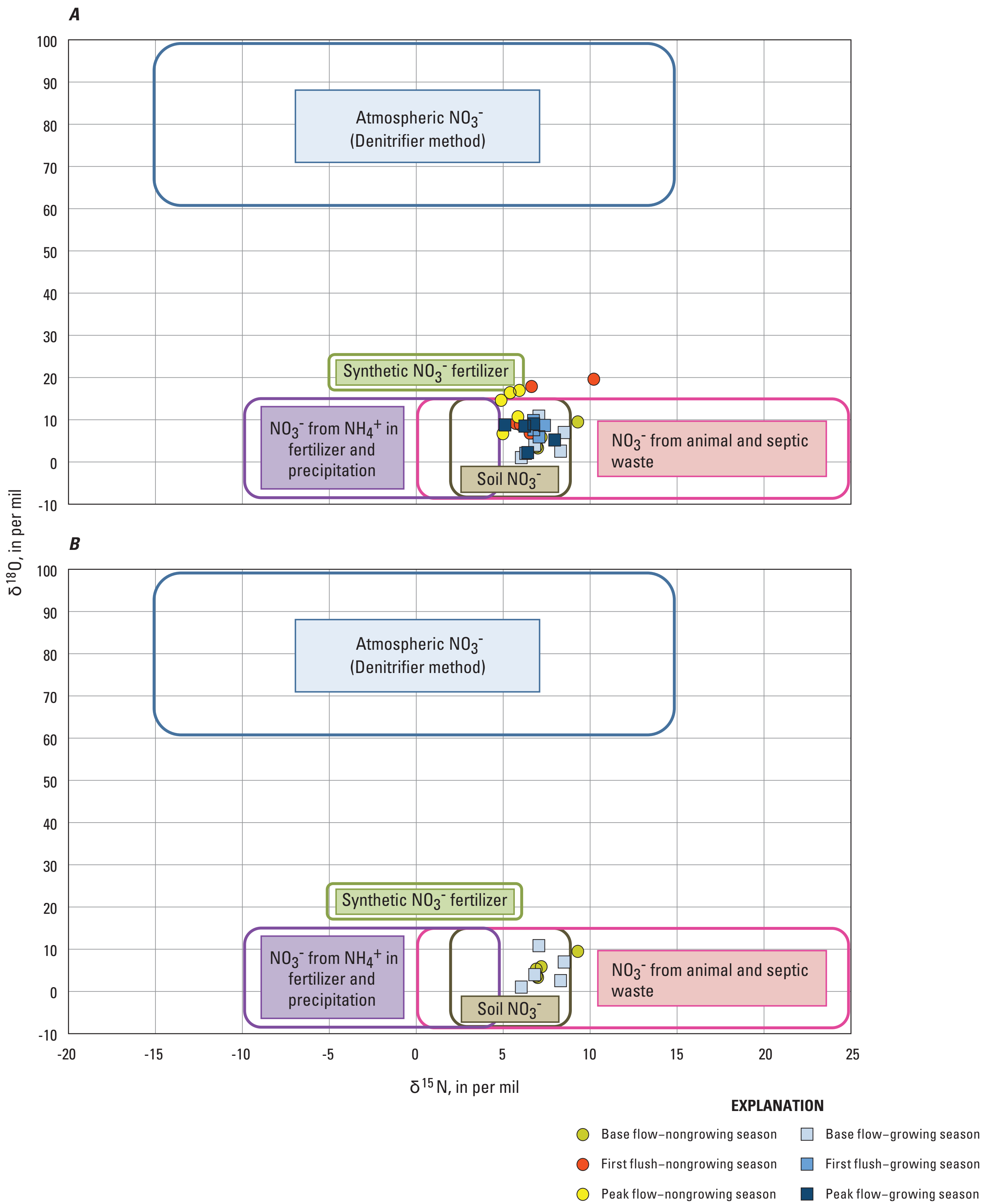

Figure 9. $\delta^{15}N$ and $\delta^{18}O$ compositions of nitrate in surface-water samples collected at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed, March–October 2010, during *A*, all flow conditions and *B*, base-flow conditions. (NO_3^-, nitrate; NH_4^+, ammonium)

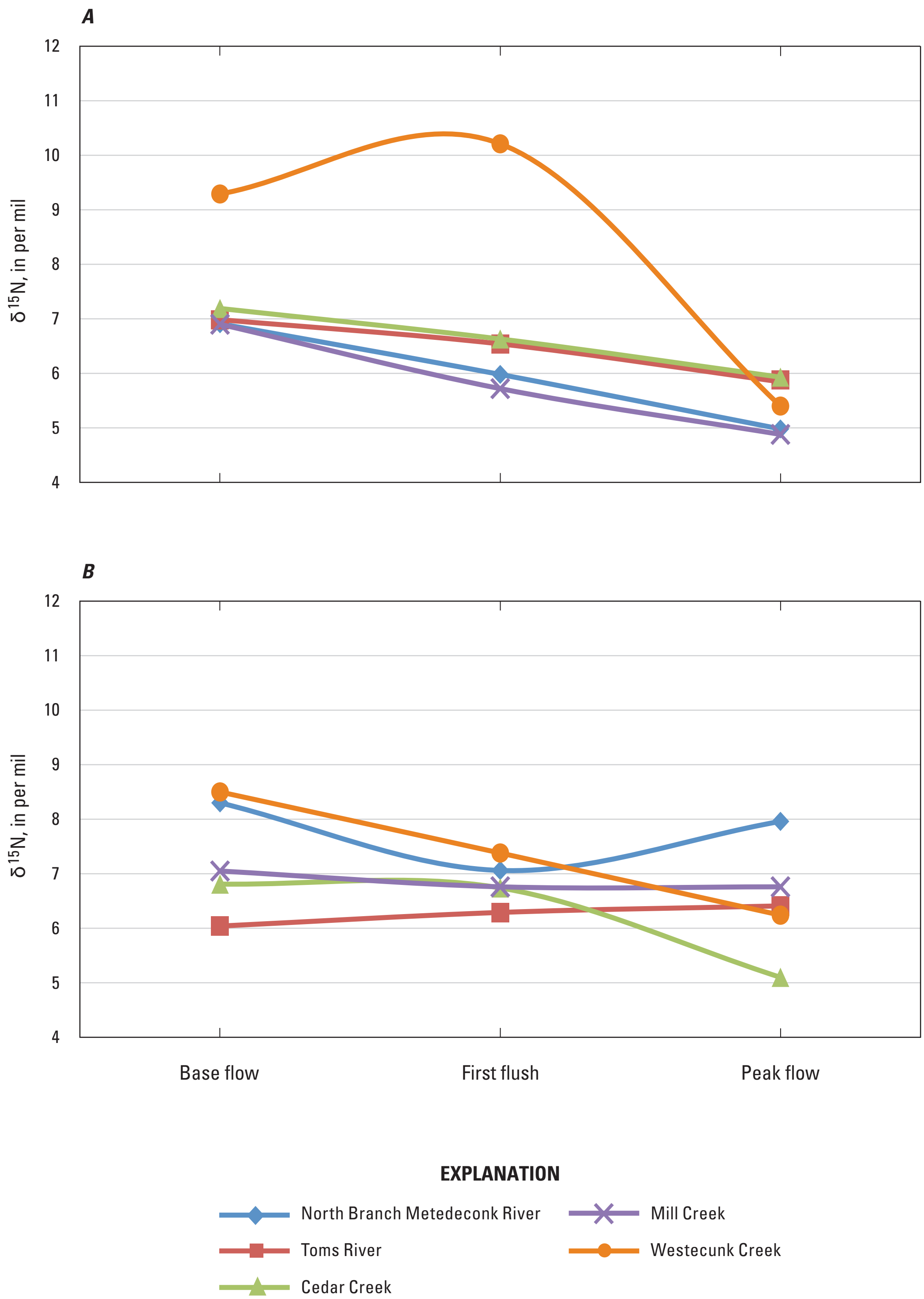

Figure 10. $\delta^{15}N$ compositions of nitrate in surface-water samples collected during base flow, first flush, and peak flow at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed during the *A*, nongrowing-season sampling event, March 2010, and *B*, growing-season sampling event, September–October 2010.

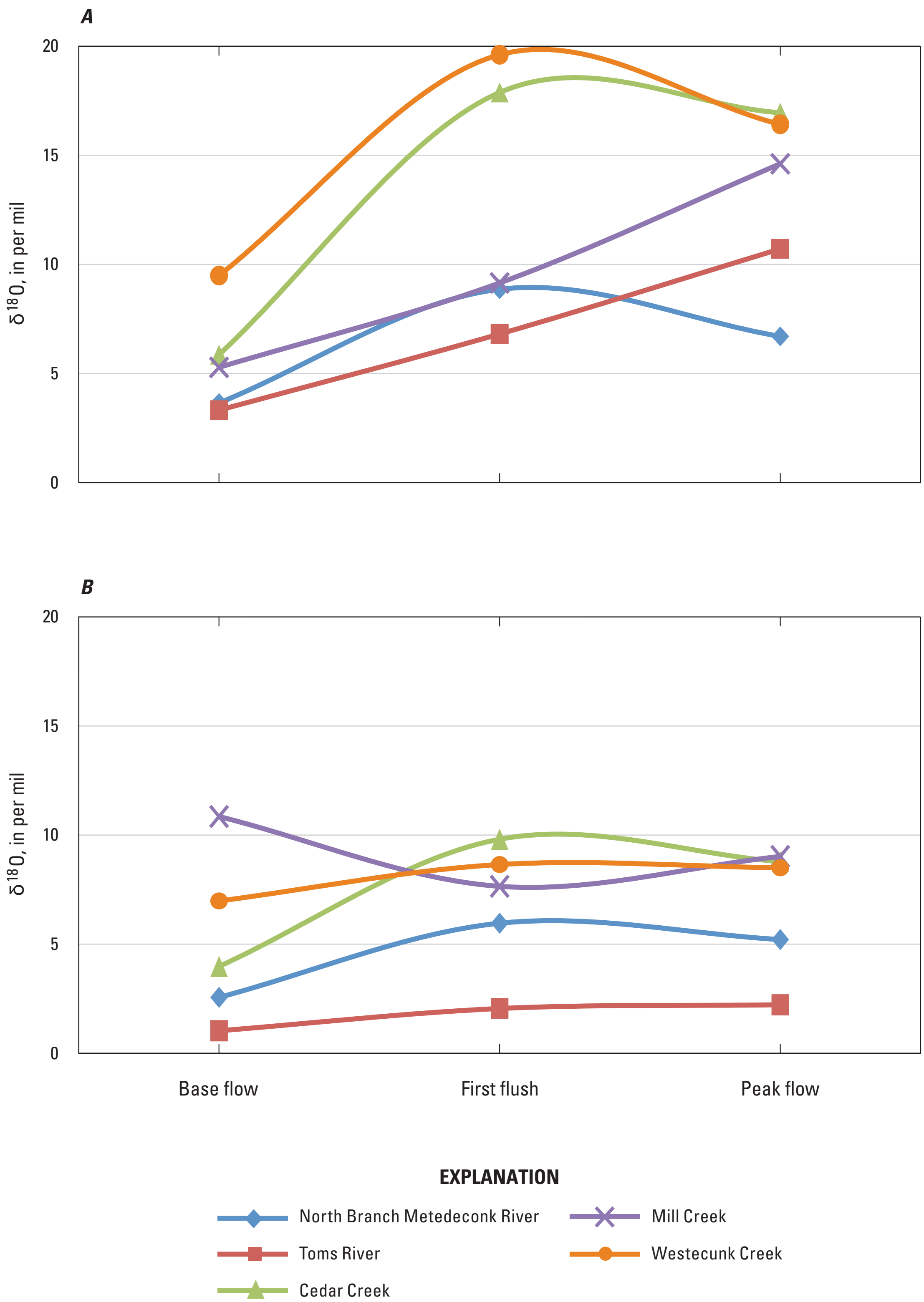

Figure 11. $\delta^{18}O$ compositions of nitrate in surface-water samples collected during base flow, first flush, and peak flow at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed during the *A*, nongrowing-season sampling event, March 2010, and *B*, growing-season sampling event, September–October 2010.

and $\delta^{18}O$ values for each of the sampling events (fig. 12). The pattern is more apparent for the nongrowing-season storm event—likely a result of the extreme hydrologic conditions at the time of sample collection, with substantial precipitation and flooding conditions during the first storm event resulting in a clearly visible pattern, and drought conditions followed by a less substantial rainfall resulting in a dampened pattern for the second event.

The $\delta^{18}O$ values by site, in order of least to most developed subbasin, are shown in figure 13A. Areas with a greater percentage of development typically have a greater percentage of impervious surface, and subsequently a greater percentage of precipitation reaching streams by way of storm runoff than do less developed areas. If atmospheric nitrate is an important source of nitrogen, there would be a positive relation between $\delta^{18}O$ values and impervious cover, such that higher $\delta^{18}O$ values occur in areas with a greater percentage of impervious cover (Silva and others, 2002). However, the lowest $\delta^{18}O$ values were measured at the Toms River and North Branch Metedeconk River stations, and 10 of the 12 samples collected at these two sites had $\delta^{18}O$ values less than the median (+8.075 ‰) for all samples collected. The nitrate concentrations in base-flow samples from these two sites were high; therefore, it would take a substantial amount of nitrate from the atmosphere to have an effect on the isotopic signature of nitrate in water from these two sites. The results indicate that although atmospheric deposition may contribute nitrate to these two subbasins, it is not a predominant source. Instead, it appears that nitrate from atmospheric sources contributes proportionally less of the overall nitrate as development increases within the BB-LEH watershed. No relation between $\delta^{15}N$ and percent urban land use is apparent (fig. 13B).

In contrast, the highest $\delta^{18}O$ values were measured in samples collected from Cedar and Westecunk Creeks, particularly during stormflow. Because these subbasins are less developed and have a lower percentage of impervious cover than do the Toms and Metedeconk River subbasins, the results indicate that atmospheric deposition of nitrate has a greater influence on these less developed subbasins within the BB-LEH watershed, likely because they contain few other major sources of nitrogen. Because the nitrate concentrations in base flow within the less developed subbasins are low, even a small contribution of nitrogen from the atmosphere has a substantial effect on the isotopic signature. Nitrate concentrations in samples from the less developed subbasins are low (less than 0.2 mg/L); therefore, the contribution from the atmosphere is minimal.

A comparison of concentrations of dissolved solids such as Cl^- and K^+ with isotope ratios can provide additional information about the likelihood of the relative importance of specific sources of nitrogen within a watershed. In a plot of the relation between concentrations of Cl^- and $\delta^{15}N$ values, it is evident that higher Cl^- concentrations at North Branch Metedeconk correspond to higher $\delta^{15}N$ values for both storm events (fig. 14A); a positive relation during both storm events is also shown at the North Branch Metedeconk River station for K^+ concentrations and $\delta^{15}N$ values (fig. 14C). The coincidence of higher $\delta^{15}N$ values with higher concentrations of dissolved solids, specifically in samples collected from the North Branch Metedeconk River during base flow, is likely a consequence of the higher degree of development within the subbasin. Higher values of $\delta^{15}N$ and Cl^- concentrations are consistent with a sewage, animal waste, or septic source (Silva and others, 2002; Mullaney and others, 2009). Within the North Branch Metedeconk River subbasin, sewage inputs could stem from leaky sewer pipes and septic systems associated with current and recent urban land use and (or) from animal waste associated with documented poultry farming that

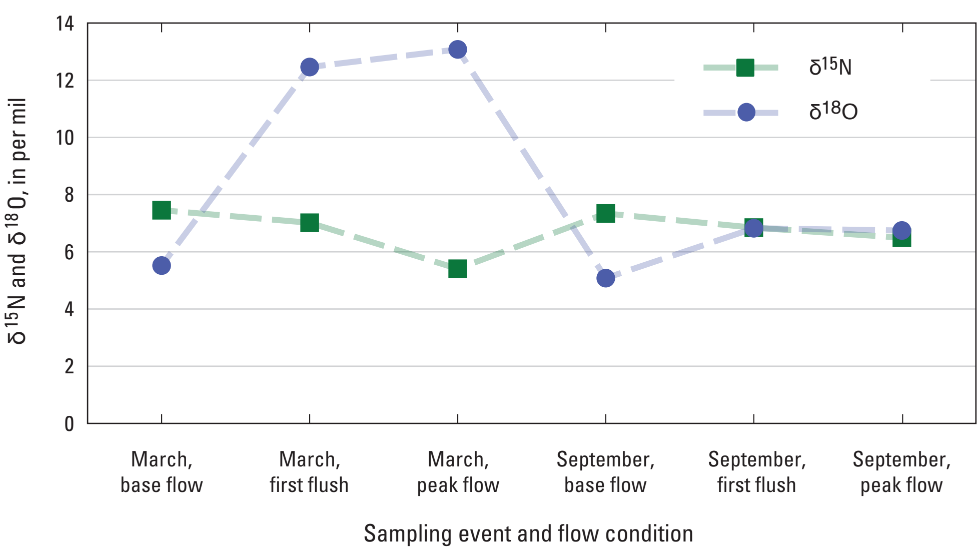

Figure 12. $\delta^{15}N$ and $\delta^{18}O$ compositions of nitrate in water at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed, averaged by sampling event and flow condition.

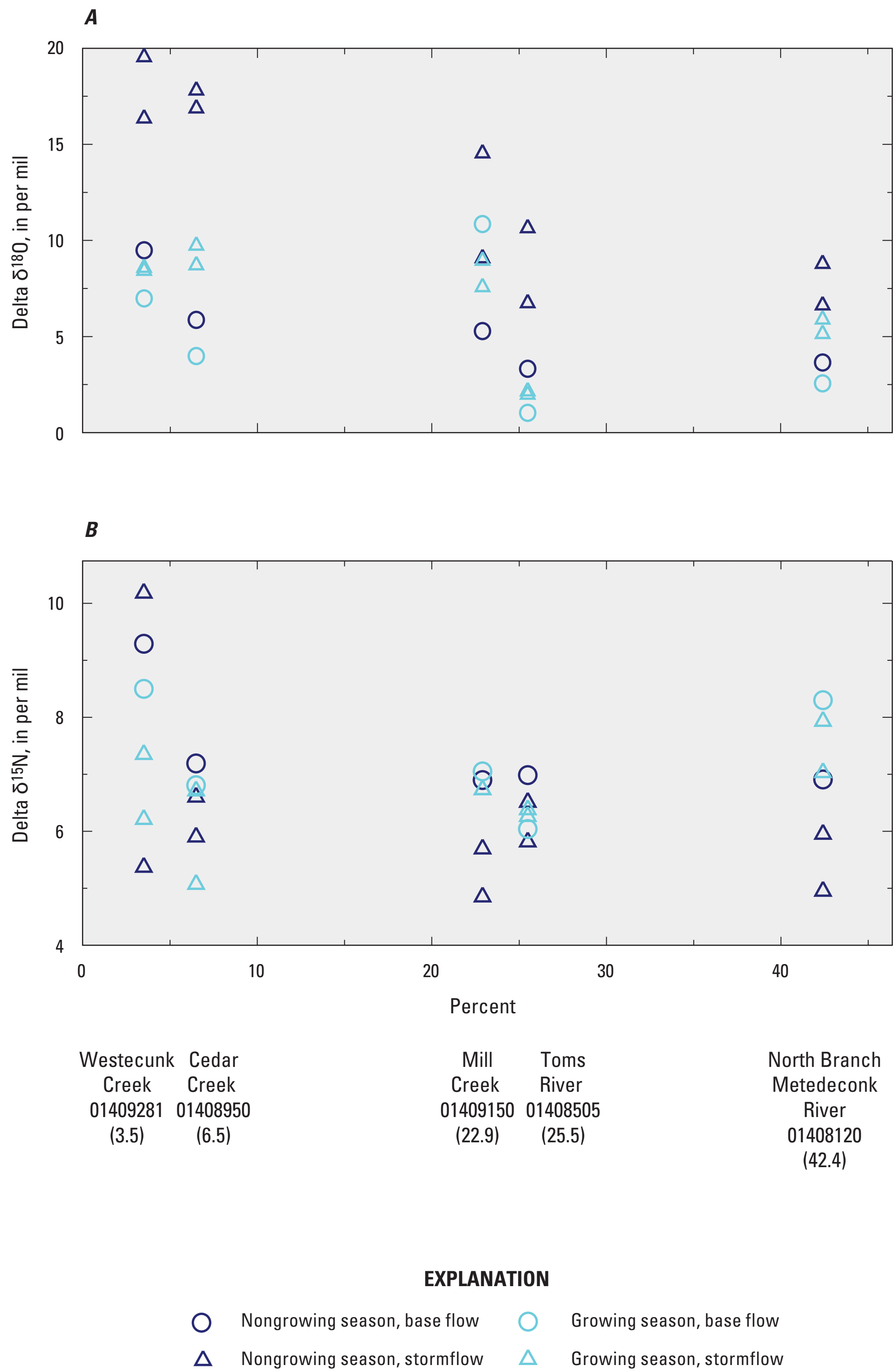

Figure 13. *A*, $\delta^{18}O$ values and *B*, $\delta^{15}N$ values in relation to percent urban land use (residential plus nonresidential, shown in parentheses) in subbasins for water-quality stations in the Barnegat Bay-Little Egg Harbor watershed.

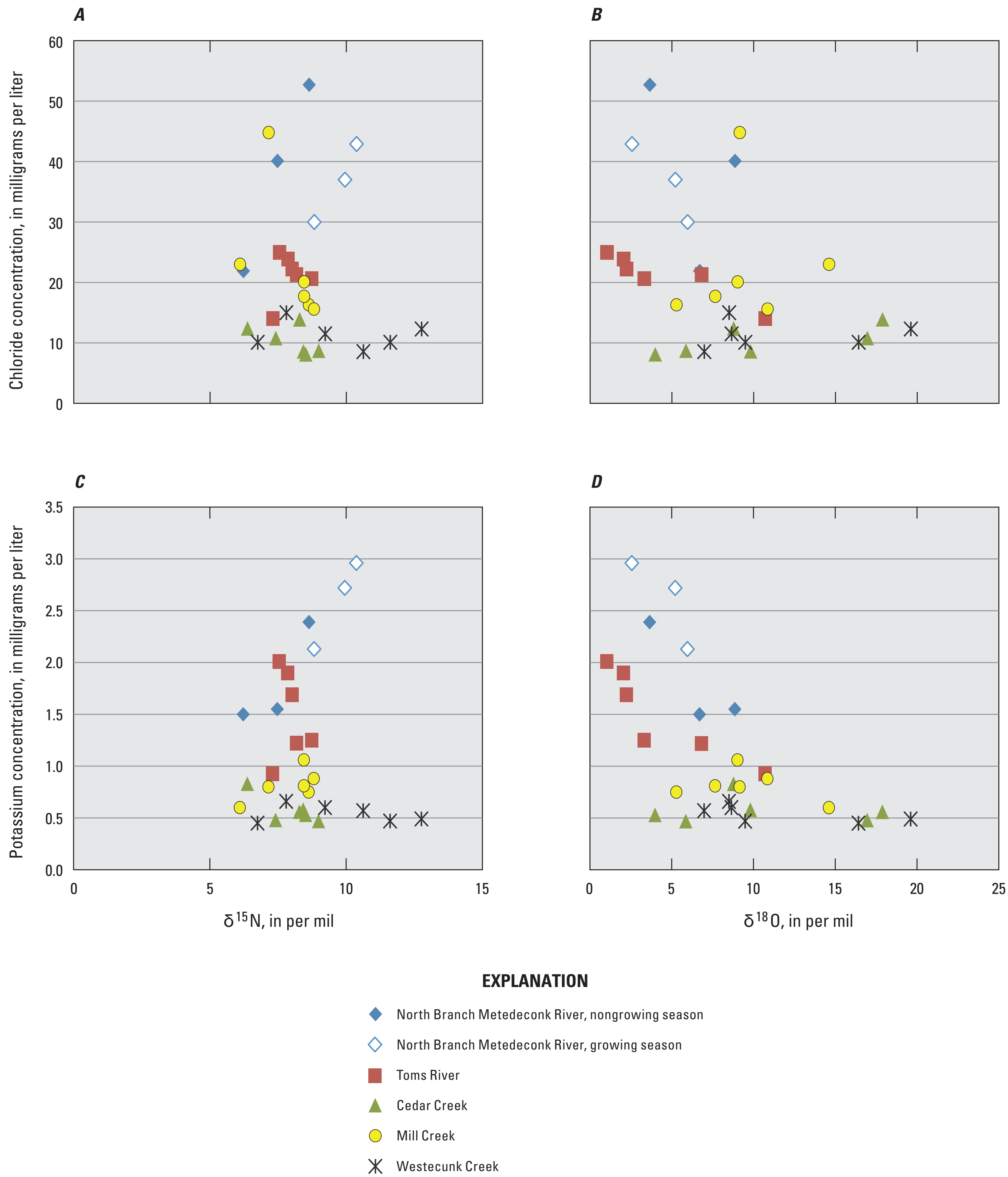

Figure 14. Relation between concentrations of water-quality constituents and isotope ratios at water-quality stations in the Barnegat Bay-Little Egg Harbor watershed: *A*, chloride concentration and $\delta^{15}N$ value, *B*, chloride concentration and $\delta^{18}O$ value, *C*, potassium concentration and $\delta^{15}N$ value, and *D*, potassium concentration and $\delta^{18}O$ value.

was historically prominent in the region (Ocean County Agriculture Development Board, 2008). Clear relations between Cl^- or K^+ concentrations and $\delta^{15}N$ values are not evident for Toms River and Mill Creek; at Cedar and Westecunk Creeks, Cl^- and K^+ concentrations are consistently low and do not vary with changes in $\delta^{15}N$ values.

In plots of the relation of Cl^- and K^+ concentrations to $\delta^{18}O$ values (fig. 14B, D), samples collected at North Branch Metedeconk River show a pattern in which higher concentrations of dissolved solids correspond to lower $\delta^{18}O$ values. A similar pattern between dissolved-solids concentrations and $\delta^{18}O$ values is evident for Toms River, although dissolved-solids concentrations are generally lower than those at the North Branch Metedeconk River station. This pattern indicates the dilution of dissolved-solids concentrations in the stream when the influence of precipitation is great. Low concentrations of dissolved solids during periods of precipitation are to be expected because atmospheric deposition does not typically contain large amounts of dissolved solids. At Cedar and Westecunk Creeks, concentrations of Cl^- and K^+ are consistently low and do not vary with changes in $\delta^{18}O$ values. Like $\delta^{15}N$ values, $\delta^{18}O$ values at Mill Creek show no clear relation with dissolved-solids concentrations, possibly as a result of a mixture of influences from recent development and undeveloped, undisturbed forested land within the Mill Creek subbasin.

Overall, the variability in $\delta^{15}N$ and $\delta^{18}O$ values and coincident variability in Cl^- and K^+ concentrations are strong evidence that the nitrate in these streams (at least in the Toms and Metedeconk Rivers) derives from a mixture of sources.

Groundwater

In a plot of $\delta^{18}O$ as a function of $\delta^{15}N$ values for groundwater samples (fig. 15), the $\delta^{15}N$ values are in the overlapping range of nitrogen originating from fertilizer, soil, and and animal and septic waste sources. Although five wells were sampled, nitrate concentrations in samples from two of the wells (290743 and 290799) were below the level necessary to conduct nitrogen and oxygen stable isotope analyses; therefore, results of stable isotope analyses are reported for only

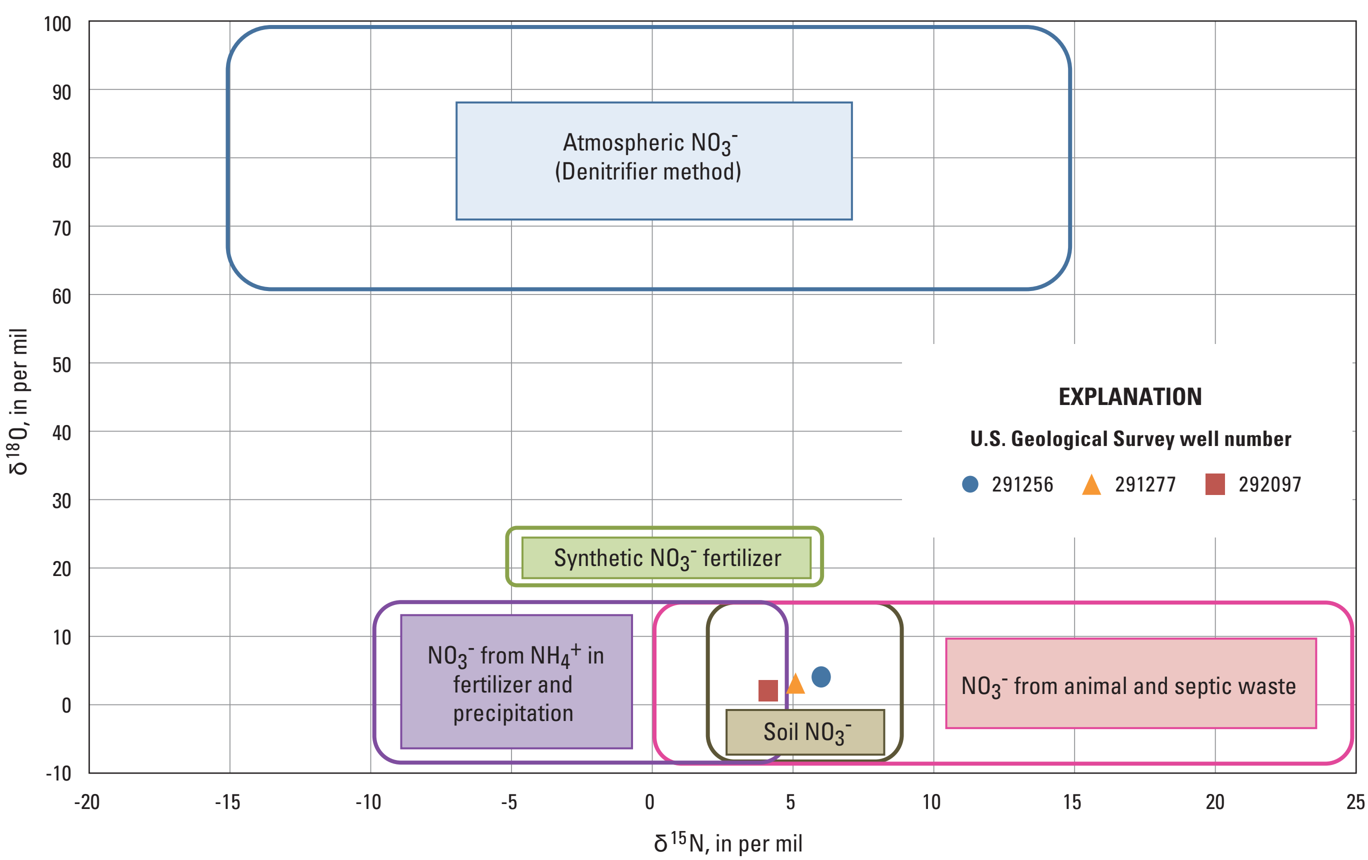

Figure 15. $\delta^{15}N$ and $\delta^{18}O$ compositions of nitrate in groundwater samples collected from shallow wells in the Barnegat Bay-Little Egg Harbor watershed, 2010–11. (NO_3^-, nitrate; NH_4^+, ammonium)

three wells. Well 292097 with a nitrate plus nitrite concentration of 2.66 mg/L had a $\delta^{15}N$ value of + 4.12 ‰, and well 291277 with a nitrate plus nitrite concentration of 3.63 mg/L had a $\delta^{15}N$ value of + 5.09 ‰ (table 7). Both of these wells are located in the northern portion of the watershed in highly developed areas; there are small pockets of farmland in the immediate vicinity of well 291277. The relatively high concentration of nitrate plus nitrite in these wells compared to those in wells in the less developed subbasins is indicative of anthropogenic sources of nitrogen, and the low to moderate $\delta^{15}N$ values, particularly at well 292097, are more consistent with fertilizer sources than with animal or septic waste, although the observed range of $\delta^{15}N$ values is indicative of a mixing of nitrogen sources. The fact that well 292097 had a high nitrate plus nitrite concentration, is relatively shallow, discharges to a major stream, and had a $\delta^{15}N$ signature more characteristic of fertilizer indicates that a portion of the nitrogen measured in streams may have originated as nitrogen-based fertilizer and been discharged to the stream in groundwater. Additional sampling of shallow groundwater is necessary to verify this hypothesis. Well 291256 had a $\delta^{15}N$ value of +6.00 ‰, indicating a slightly greater influence from animal and septic waste sources than at the northern two wells. However, the nitrate plus nitrite concentration at this site (0.29 mg/L) is low; therefore, any contribution from animal or septic waste is minimal. The $\delta^{18}O$ values for samples from each of these three wells is low (+2.07 to +4.07 ‰), indicating that atmospheric nitrate is not a major contributor of nitrogen to the water in these wells and not a major source of nitrogen within the underlying aquifer.

Summary and Conclusions

The Barnegat Bay-Little Egg Harbor (BB-LEH) estuary is a shallow, lagoonal-type estuary located along the central coast of New Jersey, separated from the Atlantic Ocean by a narrow complex of barrier islands. Physical characteristics of the estuary, including its shallow depth and poor flushing, render it particularly susceptible to the effects of nutrient loading; consequently, the ecological health of the estuary has deteriorated over the last few decades. Most point sources of nutrients have been eliminated from the BB-LEH watershed; therefore, the main contributors of nutrients to the BB-LEH estuary are nonpoint sources that can be attributed to either current or historical land uses.

The U.S. Geological Survey, in cooperation with the Barnegat Bay Partnership, sampled five streams and five wells in the BB-LEH watershed for determination of nutrient concentrations and stable isotope composition to help quantify and identify sources of nutrient loading to the estuary. From March to October 2010, streamflow and surface-water-quality data were collected in five streams or tributaries to the estuary—North Branch Metedeconk River, Toms River, Cedar Creek, Mill Creek, and Westecunk Creek. Surface-water-quality samples were collected during periods of base flow and stormflow over two sampling events, one each in the growing and nongrowing seasons.

Concentrations of total nitrogen in these five streams appear to be related to land use, such that streams in subbasins characterized by extensive urban development (and historical agricultural land use)—North Branch Metedeconk and Toms Rivers—exhibited the highest total nitrogen concentrations (0.84–1.36 milligrams per liter (mg/L) in base flow). The two streams in subbasins with the least development—Cedar Creek and Westecunk Creek—exhibited the lowest total nitrogen concentrations (0.16–0.26 mg/L in base flow).

Base-flow total nitrogen concentrations in the highly developed North Branch Metedeconk and Toms River subbasins were dominated by nitrate (59–85 percent of total nitrogen); nitrate concentrations decreased during storm events as a result of dilution by storm runoff. The contribution of nitrate plus nitrite at these two sites was generally lower during the nongrowing-season event than during the growing-season event, which may be explained by the influence of dilution from recent recharge on the nongrowing-season sample, dilution from the larger precipitation event, or a reduced contribution from fertilizer application during the nongrowing season.

Ammonia is present in trace amounts under most flow conditions in all streams except Mill Creek. In Mill Creek, ammonia makes up, on average, 60 percent of the base-flow total nitrogen concentration. Elevated concentrations of ammonia in this stream are likely associated with leachate from a landfill located upstream.

Organic nitrogen is the dominant species of nitrogen in nearly all samples collected from Cedar and Westecunk Creeks, and in all stormflow samples collected from Mill Creek (base flow at this site is dominated by ammonia). Stormflow concentrations of organic nitrogen generally were greater than those in base flow and, in some cases, made up more than 75 percent of the total nitrogen in stormflow samples from Cedar, Mill, and Westecunk Creeks. The subbasins of these streams are the least developed and a large proportion (more than 80 percent) of their areas lies within the Pinelands Area, indicating the likelihood that natural inputs of organic nitrogen to the streams increase during periods of storm runoff.

Total phosphorus and orthophosphate were not detected in most of the surface-water samples, with the exception of those collected from the North Branch Metedeconk River, where concentrations ranged from 0.02 to 0.09 mg/L for total phosphorus and 0.008 to 0.011 mg/L for orthophosphate. The absence of substantial concentrations of phosphorus in the samples collected indicates that the streams may be phosphorus-limited under some conditions.

Measurements of nitrogen and oxygen stable isotope ratios (^{15}N:^{14}N and ^{18}O:^{16}O) of nitrate in surface-water samples revealed that a mix of subsurface sources, including animal and septic waste, soil nitrogen, and commercial fertilizers, likely contributes to the base-flow nitrogen load. The results also indicate that atmospheric deposition is not a predominant source of nitrogen transported to the BB-LEH estuary from the watershed, although this does not preclude the possibility of substantial contribution of atmospheric nitrate directly to the estuary surface. The contribution of nitrate in the watershed from the atmosphere increases during stormflow. Over the two sampling events, $\delta^{15}N$ values ranged from +6.04 to +9.29 per mil (‰) during base flow. There was an overall decrease in $\delta^{15}N$ values at all sites over the course of the nongrowing-season storm, and at the Cedar and Westecunk Creek sites during the growing-season storm. The lower $\delta^{15}N$ values indicate a greater influence of nitrogen that originated as atmospheric nitrate, as ammonium in fertilizer or in precipitation, as synthetic nitrate fertilizer, or some combination thereof, and a smaller influence of animal and septic waste during stormflow than during base flow.

Over the two sampling events, $\delta^{18}O$ values ranged from +1.03 to +10.85 ‰ during base flow and from +2.05 to +19.61 ‰ during stormflow. Overall, $\delta^{18}O$ values increased at all sites over the course of the nongrowing-season storm and increased, although to a lesser degree, at all sites except Mill Creek during the growing-season storm. The higher $\delta^{18}O$ values during stormflow indicate a greater influence of nitrogen from the atmosphere during stormflow than during base flow. The highest $\delta^{18}O$ values occurred at Cedar and Westecunk Creeks during stormflow. The results indicate that atmospheric deposition of nitrate has a greater influence on these less developed subbasins within the BB-LEH watershed, likely because there are few other major sources of nitrogen (animal and septic waste, fertilizers) in the less developed subbasins. Nitrate from atmospheric sources appears to contribute proportionally less of the overall nitrate as development increases within the BB-LEH watershed. The nitrate concentrations in base-flow samples from the North Branch Metedeconk and Toms River basins were high; therefore, it would take a substantial amount of nitrate from the atmosphere to affect the isotopic signature of nitrate in water from these two sites.

The shift from higher $\delta^{15}N$ and lower $\delta^{18}O$ values during base-flow conditions to lower $\delta^{15}N$ and higher $\delta^{18}O$ values as the storms progress and flows increase is greatest in the subbasins with the lowest nitrate concentrations, which is to be expected if atmospheric nitrate is responsible for this pattern. The pattern is more apparent for the nongrowing-season storm event, likely as a result of the extreme hydrologic conditions at the time of sample collection brought on by substantial precipitation and flooding conditions.

Dissolved-solids concentrations and isotope ratios were compared to help provide additional information about the likelihood of the occurrence of specific sources of nitrogen within a watershed. Concentrations of dissolved solids (chloride (Cl^-) and potassium (K^+)) in base flow were highest in samples collected at the North Branch Metedeconk River station (greater than 42 mg/L for Cl^- and greater than 2.3 mg/L for K^+). The North Branch Metedeconk River was the only site at which there was a strong correlation between dissolved-solids concentrations and stable isotope ratios. In general, higher Cl^- and K^+ concentrations in the North Branch Metedeconk River correspond to higher $\delta^{15}N$ values. Higher $\delta^{15}N$ values and higher Cl^- concentrations are both consistent with a sewage, animal waste, or septic source.

In addition to the surface-water samples, groundwater samples were collected from five wells located within the BB-LEH watershed and screened in the unconfined Kirkwood-Cohansey aquifer system. Concentrations of nitrate plus nitrite ranged from not detected to 3.63 mg/L, with higher concentrations occurring in the highly developed northern portion of the watershed. In the two wells in which the nitrate concentration was not detected, dissolved-oxygen levels were extremely low (0.2–0.3 mg/L), indicating an anoxic environment that may have led to nitrate losses through denitrification. The two wells with the highest nitrate concentrations had low $\delta^{15}N$ values of +4.12 and +5.09 ‰. The relatively high concentration of nitrate plus nitrite in these wells compared to those in wells in the less developed subbasins indicates anthropogenic sources of nitrogen, and the low to moderate $\delta^{15}N$ values, particularly at well 292097, are more consistent with fertilizer sources than with animal or septic waste. Total phosphorus was not found at detectable concentrations in any of the wells sampled, and orthophosphate was either not detected or measured at very low concentrations (less than 0.010 mg/L).

Through the collection of hydrologic, water-quality, and stable isotope data for major streams, streams with little available data, and representative wells in the BB-LEH watershed, this study addressed several key data gaps in the understanding of nutrient dynamics in the watershed. The collection of surface-water data from subbasins with varying degrees of development and under varying hydrologic conditions allows for a more accurate determination of the spatial and temporal variability of nutrient loading throughout the watershed than could have been made previously. Stable isotope analyses revealed that a mixture of subsurface sources of nitrate from some combination of animal and septic waste, soil nitrogen, and commercial fertilizers likely contributes to the base-flow nitrogen load, and that atmospheric deposition is not a predominant source of nitrogen transported to the estuary from the watershed. The analysis of samples collected at downstram locations on five major streams in this study improved current understanding of nitrogen concentrations and sources on a broad scale for a large portion of the watershed. One limitation of the sampling design is that the contributing area for the surface-water samples contained a mixture of land uses and, therefore, a mixture of nitrogen sources. Future monitoring efforts may include stable isotope sampling in smaller subbasins dominated by single land uses to improve understanding of the relation between specific land uses and their isotopic signatures within the watershed. Analysis of such samples would help to further characterize the relative importance of terrestrial nitrate sources—animal and septic waste, soil nitrogen, and commercial fertilizers—and aid in prioritizing strategies for reducing nutrient loads such as controlling development, reducing application of commercial fertilizers, and implementing stormwater management.

Given that many of the higher concentrations of nitrate were measured in groundwater samples and in surface-water samples collected during base flow, effective monitoring strategies would include extensive groundwater sampling, as recent information on nutrient concentrations in shallow groundwater is extremely limited. Additionally, sampling along groundwater flow paths would provide information about the role of denitrification in the system.

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Appendix

Appendix 1. Summary statistics of continuous water-quality data, Barnegat Bay-Little Egg Harbor watershed, 2010.

Appendix 1. Summary statistics of continuous water-quality data, Barnegat Bay-Little Egg Harbor watershed, 2010.

[˚C, degrees Celsius; µS/cm, microsiemens per centimeter at 25˚C; mg/L, milligrams per liter; NTU, nephelometric turbidity units; --, not available]

Statistic	Temperature (˚C)	Specific conductance (µS/cm)	pH	Dissolved oxygen (percent of saturation)	Dissolved oxygen (mg/L)	Turbidity (NTU)
01408120 North Branch Metedeconk River near Lakewood, NJ, nongrowing season, March 2010, base flow						
Lowest value	8.4	234	6.46	88.9	10.13	3.4
1st quartile	9.0	236	6.53	89.3	10.21	3.8
Mean	9.5	236	6.53	90.6	10.35	4.1
Median	9.5	236	6.54	89.9	10.32	4.1
3rd quartile	10.0	236	6.54	92.0	10.49	4.3
Highest value	10.1	241	6.54	93.7	10.65	8.8
Number of observations	327	327	327	327	327	327
Standard deviation	0.5	1	0.01	1.6	0.17	0.5
01408120 North Branch Metedeconk River near Lakewood, NJ, nongrowing season, March 2010, stormflow						
Lowest value	6.7	87	5.82	84.5	10.20	3.9
1st quartile	7.2	97	5.84	86.6	10.35	9.3
Mean	7.5	148	6.10	87.2	10.45	14.1
Median	7.4	124	5.90	87.0	10.43	14.4
3rd quartile	7.9	186	6.47	87.4	10.50	17.8
Highest value	8.8	277	6.56	89.9	10.79	38.7
Number of observations	832	832	832	832	832	832
Standard deviation	0.5	59	0.30	0.9	0.13	5.5
01408120 North Branch Metedeconk River near Lakewood, NJ, growing season, September–October 2010, base flow						
Lowest value	18.6	216	6.58	85.5	7.99	1.0
1st quartile	18.8	216	6.63	86.8	8.08	1.2
Mean	18.9	216	6.67	88.2	8.19	1.4
Median	19.0	216	6.68	88.4	8.19	1.4
3rd quartile	19.1	217	6.72	89.5	8.29	1.5
Highest value	19.1	217	6.79	90.3	8.35	7.1
Number of observations	201	201	201	201	201	201
Standard deviation	0.2	0	0.05	1.5	0.11	0.5
01408120 North Branch Metedeconk River near Lakewood, NJ, growing season, September–October 2010, stormflow						
Lowest value	18.5	145	6.34	80.3	7.34	1.3
1st quartile	19.1	168	6.45	81.8	7.44	6.3
Mean	19.5	183	6.51	83.3	7.66	10.0
Median	19.4	183	6.50	83.1	7.62	9.5
3rd quartile	20.0	195	6.56	84.9	7.87	13.5
Highest value	20.2	236	6.69	85.9	8.03	39.2
Number of observations	374	374	374	374	374	369
Standard deviation	0.6	20	0.08	1.6	0.22	5.8

Appendix 1. Summary statistics of continuous water-quality data, Barnegat Bay-Little Egg Harbor watershed, 2010.—Continued

[˚C, degrees Celsius; µS/cm, microsiemens per centimeter at 25˚C; mg/L, milligrams per liter; NTU, nephelometric turbidity units; --, not available]

Statistic	Temperature (˚C)	Specific conductance (µS/cm)	pH	Dissolved oxygen (percent of saturation)	Dissolved oxygen (mg/L)	Turbidity (NTU)
01408505 Toms River at park footbridge, near Toms River, NJ, nongrowing season, March 2010, base flow						
Lowest value	8.9	106	5.10	90.7	10.40	0.8
1st quartile	9.0	107	5.15	92.0	10.45	1.0
Mean	9.5	107	5.17	92.6	10.60	1.1
Median	9.5	107	5.18	92.4	10.60	1.0
3rd quartile	10.0	107	5.19	93.6	10.68	1.0
Highest value	9.8	108	5.22	94.7	10.90	5.8
Number of observations	353	353	353	353	353	353
Standard deviation	0.2	0	0.02	1.0	0.10	0.4
01408505 Toms River at park footbridge, near Toms River, NJ, nongrowing season, March 2010, stormflow						
Lowest value	7.4	67	4.31	84.6	10.10	1.7
1st quartile	8.0	71	4.32	85.6	10.15	4.0
Mean	8.0	85	4.62	87.4	10.30	6.3
Median	7.9	77	4.35	86.1	10.20	7.0
3rd quartile	8.0	99	5.00	88.3	10.50	8.0
Highest value	9.2	111	5.41	94.3	11.20	10.8
Number of observations	1,390	1,390	1,390	1,390	1,390	1,387
Standard deviation	0.4	15	0.39	2.7	0.30	2.1
01408505 Toms River at park footbridge, near Toms River, NJ, growing season, September–October 2010, base flow						
Lowest value	19.1	135	6.32	86.5	8.00	1.4
1st quartile	19.3	136	6.35	87.5	8.07	1.7
Mean	19.5	136	6.39	90.3	8.30	1.8
Median	19.4	136	6.39	90.2	8.29	1.8
3rd quartile	19.7	137	6.43	93.2	8.53	1.9
Highest value	19.7	138	6.48	95.1	8.71	3.8
Number of observations	201	201	201	201	201	201
Standard deviation	0.2	1	0.04	2.8	0.22	0.3
01408505 Toms River at park footbridge, near Toms River, NJ, growing season, September–October 2010, stormflow						
Lowest value	17.5	119	5.64	85.7	7.71	1.8
1st quartile	19.2	126	6.16	86.6	7.95	2.8
Mean	19.5	130	6.19	87.6	8.04	4.4
Median	19.5	129	6.28	86.9	8.01	3.2
3rd quartile	19.8	134	6.30	88.0	8.13	5.4
Highest value	20.5	141	6.34	93.1	8.53	16.5
Number of observations	1,492	1,492	1,492	1,492	1,492	1,492
Standard deviation	0.6	5	0.17	1.6	0.17	2.3

Appendix 1. Summary statistics of continuous water-quality data, Barnegat Bay-Little Egg Harbor watershed, 2010.—Continued

[˚C, degrees Celsius; µS/cm, microsiemens per centimeter at 25˚C; mg/L, milligrams per liter; NTU, nephelometric turbidity units; --, not available]

Statistic	Temperature (˚C)	Specific conductance (µS/cm)	pH	Dissolved oxygen (percent of saturation)	Dissolved oxygen (mg/L)	Turbidity (NTU)
01408950 Cedar Creek at abandoned RR bridge, near Lanoka, NJ, nongrowing season, March 2010, base flow						
Lowest value	7.8	59	4.05	87.9	10.08	0.7
1st quartile	8.6	60	4.06	88.2	10.17	0.8
Mean	9.1	60	4.07	90.8	10.47	1.4
Median	9.2	60	4.06	89.6	10.33	0.9
3rd quartile	9.6	60	4.07	92.7	10.69	1.5
Highest value	9.7	61	4.17	106.7	12.59	6.4
Number of observations	307	307	307	307	307	307
Standard deviation	0.5	0	0.02	3.2	0.38	1.6
01408950 Cedar Creek at abandoned RR bridge, near Lanoka, NJ, nongrowing season, March 2010, stormflow						
Lowest value	6.8	59	3.92	90.3	10.72	0.9
1st quartile	7.4	61	3.95	92.9	11.13	2.3
Mean	7.6	69	3.98	94.1	11.24	4.2
Median	7.6	67	3.96	94.0	11.21	3.1
3rd quartile	7.9	73	3.99	94.8	11.36	5.3
Highest value	8.4	91	4.12	99.7	11.75	28.7
Number of observations	1,402	1,402	1,402	1,402	1,402	1,399
Standard deviation	0.4	9	0.04	1.9	0.21	3.0
01408950 Cedar Creek at abandoned RR bridge, near Lanoka, NJ, growing season, September–October 2010, base flow						
Lowest value	19.0	43	4.52	99.9	9.15	0.5
1st quartile	19.3	43	4.54	102.5	9.44	0.6
Mean	19.4	44	4.57	103.8	9.56	0.8
Median	19.4	44	4.57	104.0	9.56	0.7
3rd quartile	19.5	44	4.58	105.2	9.69	0.9
Highest value	19.6	45	4.70	106.2	9.84	1.9
Number of observations	229	229	229	229	229	229
Standard deviation	0.1	1	0.03	1.5	0.15	0.2
01408950 Cedar Creek at abandoned RR bridge, near Lanoka, NJ, growing season, September–October 2010, stormflow						
Lowest value	16.4	45	4.06	105.6	9.79	0.5
1st quartile	19.1	46	4.36	109.9	10.10	0.9
Mean	19.3	54	4.42	112.8	10.40	2.8
Median	19.6	47	4.50	112.7	10.43	1.5
3rd quartile	19.8	56	4.52	115.8	10.59	2.6
Highest value	20.6	87	4.79	119.8	11.11	52.3
Number of observations	1,496	1,496	1,496	1,496	1,496	1,493
Standard deviation	1.0	13	0.18	3.3	0.31	4.5

Appendix 1. Summary statistics of continuous water-quality data, Barnegat Bay-Little Egg Harbor watershed, 2010.—Continued

[˚C, degrees Celsius; µS/cm, microsiemens per centimeter at 25˚C; mg/L, milligrams per liter; NTU, nephelometric turbidity units; --, not available]

Statistic	Temperature (˚C)	Specific conductance (µS/cm)	pH	Dissolved oxygen (percent of saturation)	Dissolved oxygen (mg/L)	Turbidity (NTU)
01409150 Mill Creek near Manahawkin, NJ, nongrowing season, March 2010, base flow						
Lowest value	8.9	81	5.61	78.9	9.03	--
1st quartile	9.3	84	5.68	82.4	9.42	--
Mean	9.7	89	5.69	85.5	9.71	--
Median	9.4	89	5.69	84.6	9.64	--
3rd quartile	10.3	93	5.70	87.0	9.86	--
Highest value	10.6	100	5.81	113.0	12.64	--
Number of observations	398	398	398	398	398	--
Standard deviation	0.6	6	0.02	5.0	0.50	--
01409150 Mill Creek near Manahawkin, NJ, nongrowing season, March 2010, stormflow						
Lowest value	8.0	50	4.72	78.9	9.18	--
1st quartile	8.3	54	4.89	82.2	9.64	--
Mean	8.4	90	5.05	84.0	9.84	--
Median	8.5	74	4.96	83.9	9.83	--
3rd quartile	8.7	122	5.20	85.8	10.04	--
Highest value	8.9	181	5.61	90.4	10.60	--
Number of observations	739	739	739	739	739	--
Standard deviation	0.2	39	0.26	2.3	0.28	--
01409150 Mill Creek near Manahawkin, NJ, growing season, September–October 2010, base flow						
Lowest value	15.1	78	5.70	79.6	7.74	0.3
1st quartile	15.7	79	5.82	80.8	7.92	0.5
Mean	16.2	79	5.83	81.9	8.06	0.9
Median	16.4	79	5.84	81.7	8.00	0.6
3rd quartile	16.7	80	5.85	82.5	8.20	0.9
Highest value	16.8	80	5.87	86.3	8.52	6.3
Number of observations	723	723	723	723	723	723
Standard deviation	0.0	0	0.00	0.0	0.00	0.0
01409150 Mill Creek near Manahawkin, NJ, growing season, September–October 2010, stormflow						
Lowest value	15.6	73	5.25	69.3	6.54	1.1
1st quartile	17.4	76	5.54	73.3	6.91	2.3
Mean	17.6	80	5.56	75.7	7.23	3.9
Median	17.9	79	5.58	74.7	7.08	3.3
3rd quartile	18.2	84	5.64	78.8	7.54	5.1
Highest value	18.6	95	5.79	84.4	8.38	12.9
Number of observations	398	398	398	398	398	398
Standard deviation	0.0	0	0.00	0.0	0.00	0.0

Appendix 1. Summary statistics of continuous water-quality data, Barnegat Bay-Little Egg Harbor watershed, 2010.—Continued

[˚C, degrees Celsius; µS/cm, microsiemens per centimeter at 25˚C; mg/L, milligrams per liter; NTU, nephelometric turbidity units; --, not available]

Statistic	Temperature (˚C)	Specific conductance (µS/cm)	pH	Dissolved oxygen (percent of saturation)	Dissolved oxygen (mg/L)	Turbidity (NTU)
01409281 Westecunk Creek at Railroad Ave, at West Creek, NJ, nongrowing season, March 2010, base flow						
Lowest value	9.0	34	4.37	86.9	9.51	0.3
1st quartile	10.1	35	4.42	87.5	9.60	0.4
Mean	10.7	36	4.42	88.4	9.82	0.5
Median	10.6	35	4.43	88.0	9.86	0.4
3rd quartile	11.3	36	4.44	88.5	9.98	0.6
Highest value	12.0	39	4.46	91.5	10.30	4.3
Number of observations	457	457	457	457	457	457
Standard deviation	0.8	1	0.02	1.2	0.23	0.3
01409281 Westecunk Creek at Railroad Ave, at West Creek, NJ, nongrowing season, March 2010, stormflow						
Lowest value	7.3	39	4.08	82.2	9.51	0.8
1st quartile	8.2	40	4.10	84.0	9.82	1.5
Mean	8.4	47	4.14	84.9	9.95	2.5
Median	8.5	46	4.13	84.5	9.93	2.1
3rd quartile	8.7	55	4.14	85.6	10.09	3.1
Highest value	9.6	56	4.37	88.2	10.33	14.9
Number of observations	1,259	1,259	1,259	1,259	1,259	1,258
Standard deviation	0.5	7	0.06	1.4	0.20	1.4
01409281 Westecunk Creek at Railroad Ave, at West Creek, NJ, growing season, September–October 2010, base flow						
Lowest value	18.2	41	5.18	77.2	7.26	1.0
1st quartile	19.0	44	5.23	81.5	7.53	1.2
Mean	19.3	46	5.27	84.9	7.83	1.3
Median	19.3	46	5.27	84.1	7.76	1.3
3rd quartile	19.7	49	5.30	87.1	8.06	1.4
Highest value	20.0	55	5.46	95.8	8.80	4.5
Number of observations	986	986	986	986	986	986
Standard deviation	0.4	3	0.05	4.2	0.38	0.3
01409281 Westecunk Creek at Railroad Ave, at West Creek, NJ, growing season, September–October 2010, stormflow						
Lowest value	19.4	42	5.04	77.2	7.02	1.3
1st quartile	19.9	46	5.16	80.3	7.26	1.5
Mean	20.3	51	5.19	83.9	7.58	1.8
Median	20.5	50	5.19	83.5	7.49	1.7
3rd quartile	20.6	53	5.22	86.5	7.83	2.0
Highest value	21.0	70	5.29	92.0	8.32	3.8
Number of observations	338	338	338	338	338	338
Standard deviation	0.5	5	0.04	4.2	0.37	0.4

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