This paper should be cited as:

Fisher, T. R., T. E. Jordan, K. W. Staver, A. B. Gustafson, A. I. Koskelo, R. J. Fox, A. J. Sutton, T. Kana, K. A. Beckert, J. P. Stone, G. McCarty, and M. Lang. 2010. The Choptank Basin in transition: intensifying agriculture, slow urbanization, and estuarine eutrophication, pps. 135-165, IN: M. J. Kennish and H. W. Paerl (eds), *Coastal Lagoons: Systems of Natural and Anthropogenic Change*, CRC Press.

7 The Choptank Basin in Transition

Intensifying Agriculture, Slow Urbanization, and Estuarine Eutrophication

Thomas R. Fisher, Anne B. Gustafson, Antti I. Koskelo, Rebecca J. Fox, Todd Kana, Kristen A. Beckert, Joshua P. Stone*
Horn Point Laboratory, Center for Environmental Science, University of Maryland
Cambridge, Maryland

Thomas E. Jordan
Smithsonian Environmental Research Center
Edgewater, Maryland

Kenneth W. Staver
Wye Research and Education Center, University of Maryland
Queenstown, Maryland

Adrienne J. Sutton
PISCO, Oregon State University
Corvallis, Oregon

Gregory McCarty and Megan Lang
U.S. Department of Agriculture
Beltsville, Maryland

CONTENTS

* Corresponding Author. Email: fisher@hpl.umces.edu.

ABSTRACT

The Choptank basin and estuary are located on the Delmarva Peninsula in the Mid-Atlantic coastal plain. The regional hydrology is characterized by nearly uniform seasonal rainfall but large seasonal variations in temperature, evapotranspiration, groundwater levels, and stream discharge. Water quality in nontidal streams is largely determined by agricultural land use and animal feeding operations, and nitrogen (N) and phosphorus (P) concentrations have been increasing for decades. Inputs from nontidal streams, together with increasing human populations and wastewater discharges, have resulted in degraded estuarine water quality, including increases in chlorophyll-*a* in surface waters and declining oxygen in bottom waters. Attempts to reduce losses of N and P from nontidal streams in agricultural areas have met with limited success. One targeted watershed in the Choptank Basin showed stabilized concentrations of base flow N, along with small decreases in base flow P, a decade after extensive application of some best management practices (BMPs) in contrast to the nearby Greensboro watershed which was not targeted for BMPs and exhibited increases in base flow N and P. An attempt to improve water quality using increased stream buffers has yet to be successful, probably because new stream buffers represented only an 11% increase over existing ones.

Based on our observations, we suggest policies to improve water quality in the Choptank basin and the Mid-Atlantic region in general. We recommend application of water quality standards at the watershed scale, reduced caps for wastewater discharges, lower fertilizer applications on agricultural areas, mandatory stream buffers and winter cover crops on farms, and banning of lawn fertilizers. Anthropogenically impacted systems, such as the Choptank and Delmarva coastal bays, require a more regulated approach at the watershed scale, with long-term monitoring to improve water quality.

Key Words: Chesapeake Bay, Choptank River, Delmarva coastal bays, eutrophication, hydrology, agriculture, wastewater

7.1 INTRODUCTION

The Choptank Basin and Estuary are components of a coastal plain tributary of Chesapeake Bay on the Delmarva Peninsula. The eutrophication of the Choptank Estuary (Fisher et al. 2006b) can be viewed as a microcosm of the eutrophication processes in Chesapeake Bay as a whole. The disturbance and degradation of both the Chesapeake Bay and the Choptank Estuary over the last few centuries have been well documented (e.g., Cooper and Brush 1993; Staver et al. 1996; Benitez 2002; Benitez and Fisher 2004; Kemp et al. 2005), and the major drivers of N and P export from the terrestrial basins to the estuaries leading to eutrophication are intensive agriculture and urbanization (Lee et al. 2001; Koroncai et al. 2003). In the mainstem Chesapeake, algal blooms are common in surface waters (Glibert et al. 1995; Harding and Perry 1997; Sellner and Fonda-Umani 1999), and oxygen is depleted in bottom waters in summer (Officer et al. 1984; Hagy et al. 2004). The Choptank Estuary is currently undergoing the same degradation (Fisher et al. 2006b) that is now routinely observed in Chesapeake Bay.

An important difference between the Choptank and the main stem of the Chesapeake Bay is the depth and stratification where initial consumption of terrestrial nutrients occurs. Nutrients (N and P) enter estuaries in rivers with considerable amounts of turbidity, and the estuarine circulation further concentrates particles near the head of an estuary in a region known as the turbidity maximum (Meade 1968). In this region, little primary production and nutrient consumption occur due to the limited availability of light in the water column (Harding et al. 1986); however, as the water clears farther downstream, phytoplankton production and nutrient consumption increase, resulting in a chlorophyll-*a* maximum (Fisher et al. 1988). The chlorophyll-*a* maximum in the Chesapeake Bay develops just south of the Bay Bridge at Annapolis, where depths are 10 to 50 m, and stratification is strong, resulting in vertical isolation of bottom waters and oxygen depletion (Officer et al. 1984; Harding et al. 1986; Fisher et al. 1988). In contrast, the chlorophyll-*a* maximum in the Choptank occurs in shallower water (5 to 15 m), with weaker stratification and less isolation of bottom waters (Berndt 1999). As a result, there is less oxygen depletion in the Choptank despite higher annual average chlorophyll-*a* concentrations of 15 to 20 μg L^{-1} at the chlorophyll-*a* maximum in the water body (Fisher et al. 2006b), compared to 10–15 μg L^{-1} in the upper Chesapeake (Harding and Perry 1997). The dinoflagellate blooms known as mahogany tides that commonly occur in the Chesapeake Bay mainstem (Glibert et al. 2001; Tango et al. 2002; Marshall et al. 2004) are still only an occasional occurrence in the Choptank Estuary. Despite the somewhat higher average chlorophyll in the Choptank, the shallower bathymetry and weaker stratification has limited hypoxia in bottom waters, although it is increasing (Fisher et al. 2006b). Oxygen conditions in the Choptank, therefore, are somewhat similar to those in Chesapeake Bay in an earlier era, and an understanding of the forcing of eutrophication in the Choptank may provide useful information on the Chesapeake and other systems undergoing eutrophication, such as the Delmarva coastal bays (Wazniak et al. 2004).

The primary sources of terrestrial nutrients in the Chesapeake Bay and the Choptank Estuary are similar. Intensive agriculture and human waste disposal provide the largest sources of N and P (Staver et al. 1996; Lee et al. 2001; Koroncai et al. 2003). Agriculture and forests are the dominant land uses in the basins of both the Choptank and mainstem bay, and population density in the Choptank (59 km^{-2} in 2000; Fisher et al. 2006b) is comparable to the other Chesapeake Basins (30 to 70 km^{-2}; Carlozo et al. 2008). However, urbanization and wastewater discharges are increasing in both areas (Fisher et al. 2006a; Williams et al. 2006), and in the Choptank the largest wastewater discharges are concentrated in density-stratified areas of the estuary (Lee et al. 2001), which are susceptible to algal blooms.

In the Choptank Basin (Figure 7.1) we have been attempting to quantify the effects of agriculture, wetlands, and hydric soils on export of N and P from the land to the estuary. There are long-term USGS measurements of hydrology (since 1948) and water chemistry (since 1964) at the gauging station near Greensboro, Maryland, and in 2004, we established 17 gauged and monitored watersheds (1 to 50 km^2) within or near the Choptank Basin with varying proportions of forest (10% to 100%), agriculture (0 to 84%), and hydric soils (15% to 97%) for the study of surface waters. We have also installed ~80 piezometers (wells sampling from a limited depth stratum) to record groundwater temperature and depth and to measure the process of denitrification of agricultural nitrate (NO_3^-) as accumulation of excess N_2 and N_2O in groundwaters. The long-term goal of these projects is to evaluate the effects on water quality of agricultural Best Management Practices (BMPs) such as stream buffers and water management of agricultural ditches.

In addition to providing an example of eutrophication in the Chesapeake region, our research in the Choptank also provides useful comparisons with the lagoonal systems that are the main

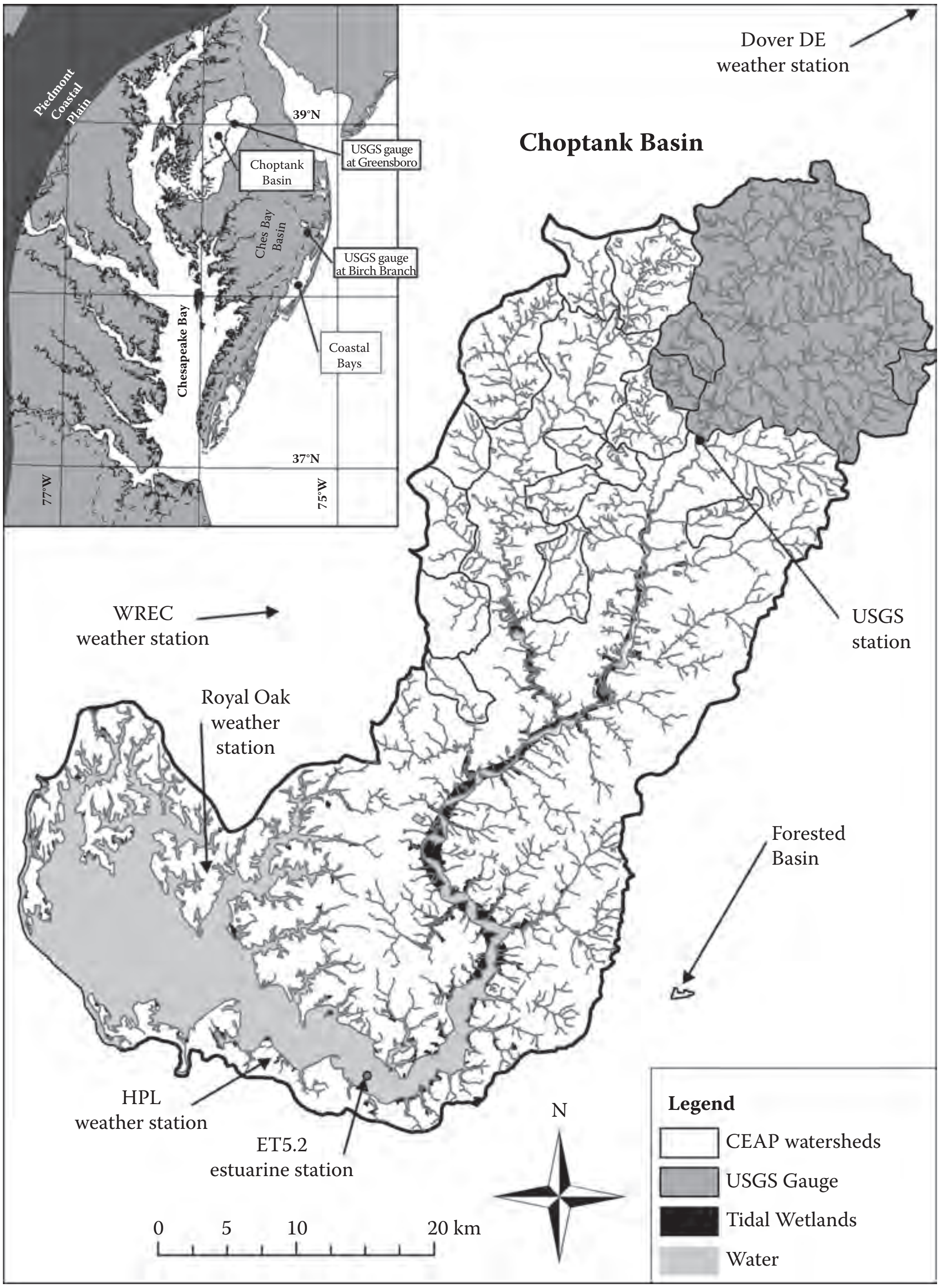


FIGURE 7.1 Inset: The location of the Choptank Basin and coastal bays on the Delmarva Peninsula in the Mid-Atlantic region of North America. Basins of two USGS gauging stations are also shown. Main figure: Choptank Basin and Estuary showing locations of weather stations, the gauged basins in and near the Choptank, and the EPA Bay Program Monitoring station ET5.2. The forested basin lies just outside the Choptank in the adjacent Nanticoke Basin.

subject of this volume. The Delmarva coastal bays are nearby (<80 km) on the eastern margin of the Delmarva Peninsula (Figure 7.1), and there are many useful parallels between the Choptank and the coastal bays. Here we summarize our research on the Choptank and attempt to relate our results to parallel observations in the basins and lagoonal systems of the Delmarva Peninsula.

The main focus of this chapter is an analysis of how anthropogenic activities on land (primarily fertilizer applications, animal waste production, and human waste disposal) influence nutrient export from land to the estuary, and how estuarine water quality responds to these nutrient inputs. We also explore attempts to reduce nutrient losses from land to estuary, and how these might be improved in the future. Most of the information is taken from the Choptank Basin, but we also compare these results with related measurements from other Delmarva basins, including the coastal bays.

7.2 STUDY SITE

The Choptank Basin (1756 km^2) and Estuary (280 km^2) are located on the eastern shore of Chesapeake Bay on the Delmarva Peninsula, a region of the Mid-Atlantic coastal plain of North America (Figure 7.1). The Delmarva Peninsula has low topographic relief (<30 m elevation) and incised nontidal stream valleys with poorly drained, hydric soils. The stream valleys are typically forested in second- and higher-order streams, and ditched in first-order streams (Norton and Fisher 2000). The land use of the adjacent uplands is usually dominated by row crops, but increasingly row crops are being converted to low density urban areas (Lee et al. 2001; Benitez and Fisher 2004, in review; Fisher et al. 2006a, 2006b for more details). Soils range from well-drained, oxic sandy loams to poorly drained clays which are usually hydric and hypoxic (Norton and Fisher 2000). Several hydrogeomorphic provinces have been described on Delmarva (Hamilton et al. 1993), consisting of the poorly drained uplands in the center of Delmarva, the well-drained lowlands, and the poorly drained lowlands close to Chesapeake Bay. Hydric soils and wetlands are more commonly found in the poorly drained uplands and lowlands than in the well-drained lowlands.

au: possible to update "in review" citation now?

The Choptank Estuary is a broad, shallow, flooded coastal plain valley with salinities of 0 to 15. The tidal region of the former river valley is ~100 km in length, and the maximum depth in a horizontally restricted portion of the estuary is ~30 m. The former river thalweg forms a narrow channel of 0.5 to 2 km in width, with typical channel depths of 5 to 10 m. Broad shallows of 1 to 5 km in width flank both sides of the channel, with depths of 0 to 3 m; numerous shallow tidal creeks penetrate far inland, particularly in the lower Choptank (Figure 7.1). The upper half of the estuary is bordered by tidal wetlands of 10 to 500 m in width, and dense stands of emergent macrophytes grow annually to high densities (Traband 2003). Sediments in the estuary are largely soft, organic-rich muds, much of which was formerly dominated by oyster bars (Newell et al. 2004).

7.3 METHODS

7.3.1 Hydrology

Data on surface water discharge were obtained from two sources. Daily discharge data were downloaded from the water website of the USGS (www.water.usgs.gov) for the gauging station near Greensboro, Maryland (01491000) in the Choptank Basin (Lee et al. 2001; Fisher et al. 2006b). The gauged watershed is 293 km^2, lies within the poorly drained uplands of Delmarva, and has been gauged since 1948 by the USGS. The Greensboro watershed contains less agriculture, more forest, and more hydric soils than the Choptank Basin as a whole (Fisher et al. 1998). In 2003, the USDA Conservation Effects Assessment Project (CEAP) selected 17 smaller watersheds (1 to 50 km^2 in area) for study of the effects of agricultural management practices on water quality. All of these watersheds lie within the Choptank Basin (Figure 7.1) except the 100% forested reference watershed, which is in the adjacent Nanticoke Basin. Two watersheds are dominated by forests, and in the remainder agriculture is the dominant land use (Table 7.1). Water discharge from the CEAP

au: please specify Fisher et al. 1998a or 1998b.

TABLE 7.1
Summary of Physical Characteristics in the 17 Gauged Watersheds of the Choptank Basin

		Land use, % of subbasin area					Hydrologic soil class, % of subbasin area				%	# CAFOs	
Subbasin	Area, km^2	Agriculture	Developed	Feedlots	Forest	CREP	A	B	C	D	Hydric	1990	2006
USGS (Greensboro)	293.3	48.9	4.6	0.4	45.7	NA	15.4	12.4	13.0	59.2	63.2	NA	NA
Kittys Corner	13.5	64.3	2.0	0.9	32.1	0.7	46.2	22.1	23.3	2.5	26.0	2	NA
Cordova	26.5	75.1	4.0	1.3	18.4	1.1	53.8	22.4	16.9	1.2	14.6	5	NA
Norwich Creek	24.5	69.6	1.8	0.4	23.1	5.2	11.7	35.7	21.7	26.5	32.6	1	NA
Blockston Branch	17.0	63.3	0.0	0.3	28.3	8.1	2.3	39.5	20.1	38.0	34.3	2	NA
Piney Branch	14.7	78.0	3.6	1.6	16.2	0.6	57.9	13.6	23.3	0.8	24.1	3	NA
Oakland	10.0	83.8	4.4	1.3	10.3	0.2	74.2	5.9	15.9	0.9	16.8	3	1
German Branch	51.4	67.8	0.2	0.9	26.8	4.2	0.7	36.6	11.7	51.0	45.2	9	NA
Beaverdam Ditch	23.3	62.3	0.8	0.0	32.2	4.6	0.7	27.9	5.3	66.1	64.1	0	NA
Long Marsh Ditch	40.5	54.1	0.4	0.5	40.8	4.2	13.7	22.3	9.5	54.5	63.7	2	NA
Broadway Branch	16.2	61.5	2.3	0.7	35.1	0.4	29.0	12.5	16.9	41.6	58.4	3	NA
Oldtown Branch	11.6	54.3	8.4	1.2	32.3	3.7	29.5	9.6	27.5	32.3	59.9	3	NA
Spring Branch	12.2	74.3	0.3	0.3	21.6	3.5	59.4	8.3	26.8	5.2	32.0	1	NA
North Forge Branch	25.0	59.6	2.1	0.2	30.7	7.4	31.0	16.8	29.8	21.0	51.2	0	NA
South Forge Branch	8.5	62.9	5.3	1.4	28.2	2.2	45.7	11.7	34.3	3.9	38.2	1	NA
Downes	23.4	76.8	5.1	1.7	15.6	0.8	66.6	11.9	19.0	0.4	19.4	6	NA
Willow Grove	8.59	24.0	0.6	0.0	75.4	0.0	0.0	0.5	2.3	97.2	97.2	NA	NA
MarshyHope Forested	0.7	0.0	0.0	0.0	100.00	0.0	50.72	49.28	0.0	0.0	54.4	0	0

watersheds was calculated from stage measurements collected at 30 minute intervals using Solinst Leveloggers (model 3001 LT F15/M5) installed in anchored cinderblocks. The raw stage data were corrected for variations in barometric pressure using a separate Solinst Barologger (model 3001 F5/M1.5). Exponential rating curves relating stage (cm) to discharge (m^3 s^{-1}) were developed from direct discharge measurements using a Gurley pygmy meter at low flows and a StreamPro ADCP during storm flows ($r^2 = 0.92$ to 0.99; Koskelo 2008; Fisher et al. unpublished).

7.3.2 Surface Water Chemistry

Surface water chemistry was sampled as both base flow and storm flow. Base flow was collected monthly as single surface grab samples during 1986 to 1987 (Norton and Fisher 2000) and during 2003 to 2008 (Sutton 2006; Sutton et al. 2009b) when there had been no rain for 3 days. Storm flow was sampled selectively during seven to eight storms in four basins during 2006 to 2007 (Koskelo 2008); samples were collected hourly using ISCO model 6700 samplers (two samples composited per bottle) over 48 hours. Sampling tubes for the ISCOs ran to a perforated tube mounted on top of the anchored cinderblocks housing the data loggers in mid-stream.

Samples were transported to the laboratory on the day of collection of base flow samples and within 24 h after the end of a storm event for storm samples. Particulates were filtered at low vacuum on tared Whatman GF/F filters, dried at 50°C, and reweighed to 0.01 mg for computation of total suspended solids (TSS, mg L^{-1}). Controls to correct for filter weight loss during handling (three per storm event) were performed using filtrate. The filtrate was also analyzed for NH_4^+, NO_2^- + NO_3^-, and PO_4^{3-} using automated colorimetric methods in the HPL Analytical Services Laboratory and in the USDA Agricultural Research Service Analytical Laboratory. Colorimetric nutrient analyses in both labs have been successfully compared using split samples and standards (McConnell and McCarty 2005). Unfiltered samples were autoclaved with persulfate oxidizing reagents to convert all forms of N and P to NO_3^- and PO_4^{3-} (Valderrama 1981). Following digestion, autoclaved samples were neutralized to pH 7 and analyzed for NO_3^- and PO_4^{3-} as described above.

7.3.3 Drainage Control Structures

Many areas of Delmarva have been ditched during the last 200 years to improve the drainage for agricultural or residential purposes (Bell 2000). Many of these ditched areas were formerly wooded wetlands on hydric soils, which were likely to have been very strong landscape sinks for anthropogenic nutrients (see below). These ditched areas now under agricultural land use are large sources of nutrients, often discharging water with N concentrations of 700 to 1000 μM (10 to 15 mg N L^{-1}) during base flow, primarily as NO_3^-. Concentrations of P during storms are 15 to 30 μM (0.5 to 1.0 mg P L^{-1}), primarily in the form of particulate P and PO_4^{3-} (Hively et al., in review).

au: possible to provide publication date now and update in reference list?

In an attempt to restore some of the former wetland function in these drained wetlands, the USDA and Maryland Department of Agriculture are installing experimental drainage control structures that enable the regulation of water level within the drainage ditches via drop-in boards. We monitored both surface waters and adjacent groundwaters (see below) of a 1-km long ditch on a farm in Caroline County, Maryland, that had a drainage control structure installed in the middle of the ditch. Groundwater levels were ~2 m below the soil surface in the original unflooded section of the ditch, but damming of surface water by the drainage control raised groundwater to ~1 m below the soil surface in soils adjacent to the flooded section of the ditch. The goals of raising the water levels in the flooded section of the ditch were to improve water availability to crops during the summer months as well as to increase the rate of denitrification of agricultural nitrate in groundwater by increasing the exposure of nitrate-rich groundwater to C-rich surface soils (for details, see Hively et al., in review). We monitored the surface chemistry of this ditch at both the end of the flooded and unflooded sections at monthly intervals to assess the impact of the drainage control

please update if possible.

structure on nitrate in ditch waters. Chemistry methods were the same as those described above for the watershed sampling.

7.3.4 Groundwater Piezometers

Groundwaters were monitored by installation of piezometers which sampled defined depth strata in ditch and wetland studies. We augured from the soil surface to depths of 1 to 4 m, and in some locations, piezometers were installed at multiple depths within a 2- to 3-m radius in order to sample vertical differences in groundwater chemistry in the top of the unconfined aquifer. We pumped piezometers dry 24 h prior to sampling to ensure fresh groundwater, and we isolated the inflowing groundwaters from exposure to the atmosphere using a sphere with a diameter of ~5 cm floating within the piezometer. After removing the float, a 5-cm Teflon bailer was lowered as deeply as possible to obtain groundwater at the bottom of the piezometer with the least exposure to the atmosphere. A Teflon stopcock and tubing were inserted into the bottom of the bailer to transfer groundwater samples from the bailer to 15-mL ground glass stoppered tubes. The Teflon tubing reached the bottom of the glass tube, and the tube was filled with one volume of overflow to reduce air exposure and eliminate bubbles. After stoppering, the tubes were stored in ice until analyses the next day to prevent bubble formation. An additional sample was transferred to a plastic bottle for colorimetric chemistry (NH_4^+, NO_3^-, PO_4^{3-}) or for electrode measurements (pH, conductivity).

Most piezometers were equipped with the same model Solinst data loggers used for stream stage. Groundwater depth and temperature in the piezometers were recorded at 30 minute intervals, and loggers were downloaded at 3- to 6-month intervals. The pressure data were corrected for variations in atmospheric pressure, as described above for the stream loggers. Groundwater depth below the soil surface was computed from variations in water depth within the piezometers and the fixed depth from the soil surface to the bottom of the piezometer.

7.3.5 Excess N_2, O_2, N_2O, and CH_4

Denitrification is an important process in groundwater which occurs under low or zero oxygen conditions, resulting in the conversion of NO_3^- into N_2 and N_2O gases. Quadruplicate ground glass stoppered tubes were used for analysis of dissolved gases (N_2, O_2, and Ar) using a Pfeiffer Vacuum model QMG422 quadrupole mass spectrometer fitted with a membrane inlet (MIMS; Kana et al. 1994, 1998; Kana and Weiss 2002). Concentrations of Ar, N_2, and O_2 in the samples (μM) were computed using sample signals (μamps) and air calibration factors (μamps/μM). Ar concentrations were used as a tracer of exchange with the atmosphere prior to and during infiltration of rainwater to groundwater, and an inverted solubility curve was used to estimate the effective recharge temperature (Figure 7.2A). We have compared these effective groundwater recharge temperatures to in situ temperatures observed at the time of collection (Figure 7.2B), and the cooler recharge temperatures indicate that most recharge occurs in fall, winter, and spring at relatively low temperatures (Figure 7.3), which agrees with direct observations of infiltration (e.g., Staver and Brinsfield 1998; Figure 7.4).

Equilibrium O_2 and N_2 concentrations were computed from their respective solubility curves in freshwater (Colt 1984) and the Ar-based recharge temperature. The equilibrium concentrations were combined with the observed N_2 and O_2 concentrations measured in the MIMS to compute excess N_2-N (μM) and % saturation of O_2 as follows:

$$\text{excess } N_2\text{-N} = 2 * (\text{observed } [N_2] - \text{equilibrium } [N_2]) \tag{7.1}$$

$$\% \text{ saturated } O_2 = 100 * (\text{observed } [O_2]/\text{equilibrium } [O_2]) \tag{7.2}$$

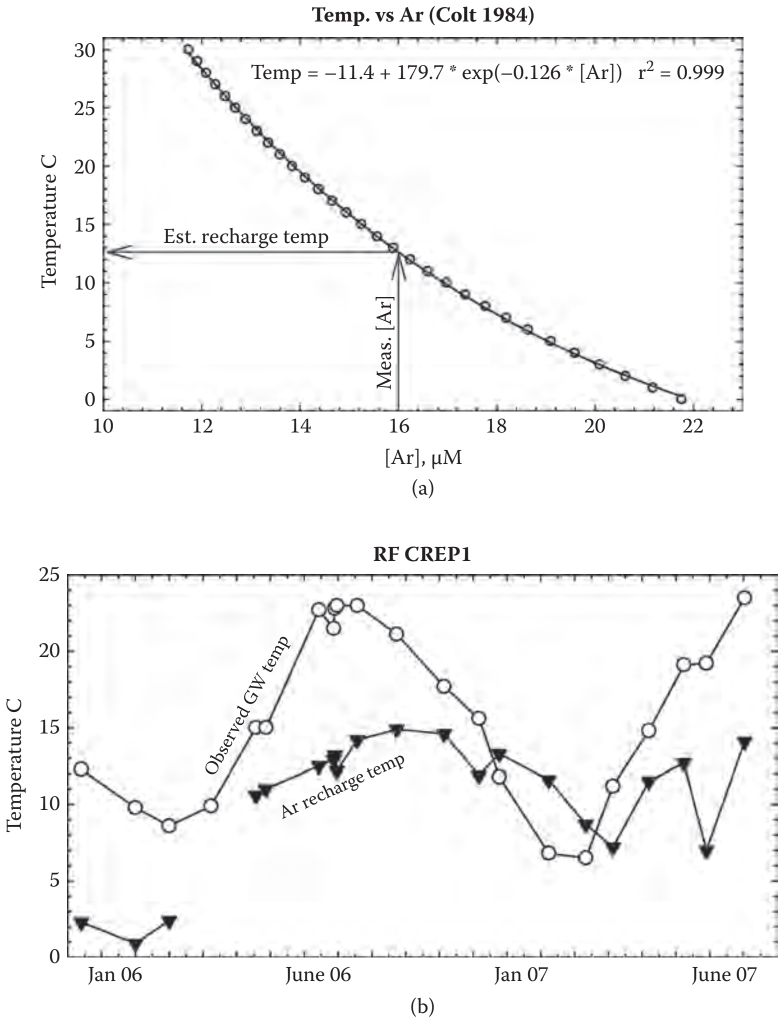
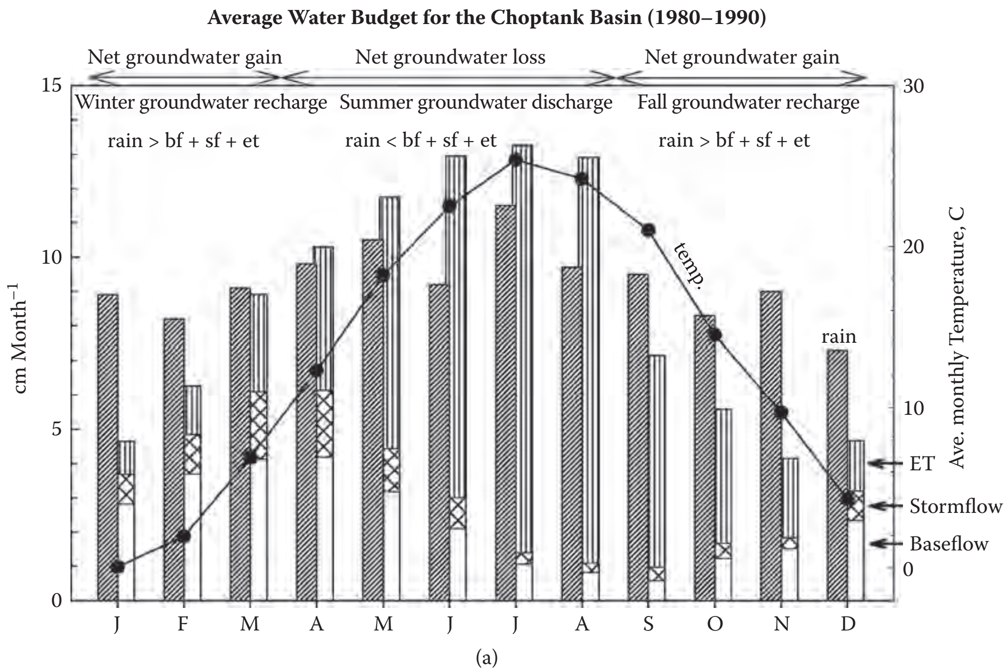


FIGURE 7.2 (a) Inverted Ar solubility curve used to estimate groundwater recharge temperatures from observed Ar concentrations. (b) Comparison of Ar recharge temperatures and observed groundwater temperatures in the top of the unconfined aquifer sampled by a piezometer within a forested buffer between an agricultural field and tidal waters. Groundwater temperature cycles annually due to heat fluxes through the soil, but the Ar recharge temperatures exhibit a damped seasonal cycle primarily reflecting the recharge history integrated over several months during cooler seasons.

Excess N_2 was expressed per unit N for comparison with NO_3-N and usually ranges from near zero to ~500 μM N_2-N (in excess of the equilibrium N_2-N of 1100 to 1500 μM, depending on recharge temperature). Excess N_2-N represents the amount of NO_3^- that has been converted to N_2 gas that is retained in the groundwater. In contrast to supersaturated N_2 in groundwater, O_2 is usually undersaturated in groundwater and varies from near-zero to 90% saturation.

The respiratory gases N_2O and CH_4 were also measured using the same groundwater sampling protocol described above. These are end-products of soil metabolism (nitrification, denitrification, and methanogenesis), and we use their concentrations to infer processes in the soil upslope of the piezometer sampling location. Aliquots of the groundwater samples were removed by syringe from the ground glass stoppered tubes and injected into 12-mL borosilicate Labco Exetainer® vials



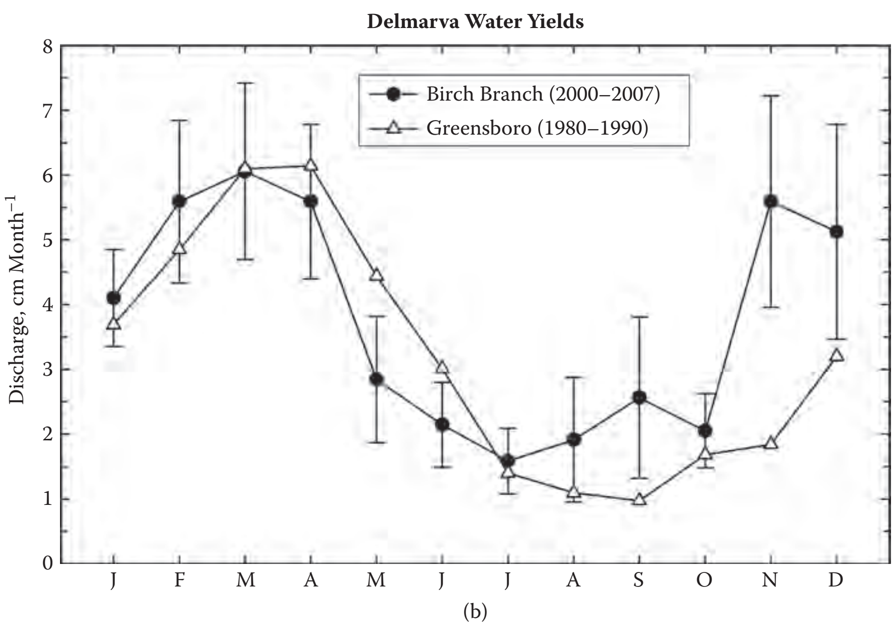


FIGURE 7.3 (a) Regional, long-term precipitation and discharge records (cm month^{-1}) for the Delmarva Peninsula based on daily data collected at NADP site MD13 at WREC, the NWS observer station at Royal Oak, Maryland, the automated NWS station at Dover, Delaware, and the Horn Point Laboratory weather station (see Figure 7.1). Base flow, storm flow, and evapotranspiration for the Choptank River at Greensboro, Maryland (USGS sta. 01491000) are from Lee et al. (2001). (b) Comparison of long-term monthly water yields (base + storm flow) at Greensboro in the Choptank River and at Birch Branch in the St. Martin Basin of the Delmarva coastal bays (USGS sta. 0148471320). Water yields are discharge (m^3 month^{-1}) normalized to basin area (m^2).

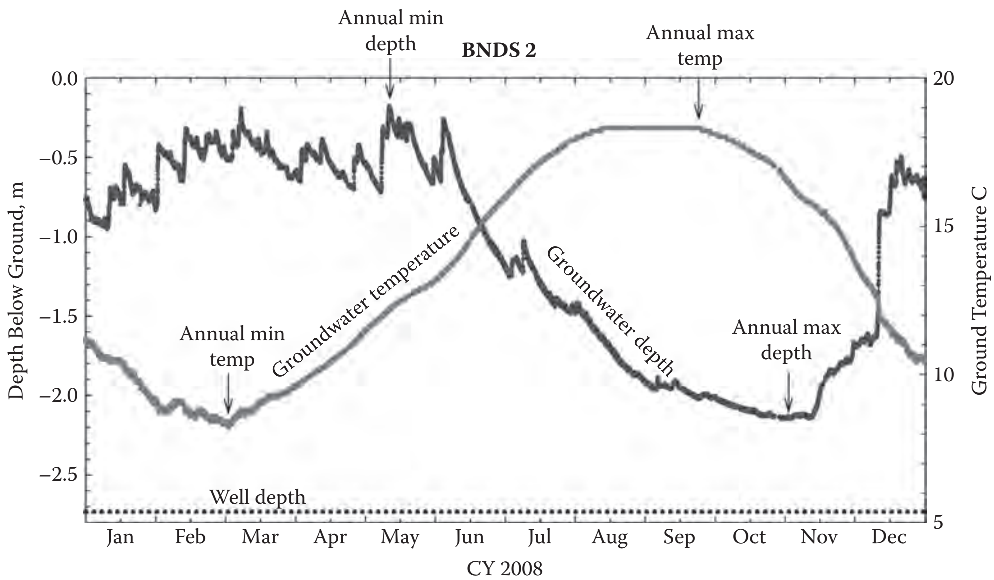


FIGURE 7.4 Annual summary of groundwater temperature and water depth below ground surface (water table depth) in a piezometer sampling the top of the surficial aquifer at 2.8 m depth below ground at a location within the basin of the USGS gauge on the Choptank River at Greensboro (see Figure 7.1). Multiple recharge events occurred in cooler months (January to May and November to December in 2008), with fewer and smaller recharge events in summer (Figure 7.3A). The overall pattern was driven by infiltration events in cooler periods and an excess of ET over recharge in summer (Figure 7.3A). Groundwater temperature exhibited a similar but inverted cycle primarily due to heat conduction through the ground from the overlying air.

previously purged with N_2 gas. The vials were manually shaken for 2 minutes to ensure full equilibration of the N_2 headspace and water. A sample of each respective headspace was injected into both a Shimadzu GC-14B equipped with an electron capture detector (ECD) with a HayeSep Q column for N_2O analysis and a separate Shimadzu GC-8A equipped with a flame ionization detector (FID) with a HayeSep A column for CH_4 analysis. The concentration of each gas was injected at a volume that lies within the linear range of each instrument, and sample concentrations were corrected for the influences of pressure, temperature, and solubility.

7.3.6 Estuarine Water Quality Data

Data for Choptank station ET5.2 (Figure 7.1) were downloaded from the Chesapeake Information Management System (CIMS, www.chesapeakebay.net/data/index.htm). The data consist of monthly vertical profiles of temperature (°C), salinity, oxygen (mg O_2 L^{-1}), chlorophyll-*a* (chl*a*, μg L^{-1}), and nutrients (NH_4^+, NO_3^-, TN, PO_4^{3-}, TP) collected by Maryland Department of Natural Resources as part of the EPA Chesapeake Bay Water Quality Monitoring Program. Here we have used the data on annual average surface chl*a* and summer (June to August) bottom dissolved oxygen (deepest depth reported) to quantify interannual trends at this station.

7.4 RESULTS

7.4.1 Regional Hydrology

The hydrology of the region is controlled by rainfall, temperature, evapotranspiration, topography, and soil drainage properties. Rainfall in the Mid-Atlantic region is relatively uniform throughout the year, and Figure 7.3A shows a climatic regional summary for 1980 to 1990. Despite the relatively uniform precipitation throughout the year (diagonally striped bars, 8 to 13 cm mo^{-1}) with a slight maximum in July, a large seasonal variation in discharge occurs (1 to 6 cm mo^{-1}) with a minimum in September due to a large seasonal variation in air temperature (0°C to 26°C); these, in turn, drive a parallel pattern of evapotranspiration (ET, 1 to 11 cm mo^{-1}) with a maximum in July, diverting rainfall back to the atmosphere as water vapor rather than discharging it as stream water (base flow + storm flow). In the warmer months with highest insolation (April to August), ET plus stream discharge exceeds rainfall, resulting in a net water loss and falling groundwater levels (Figure 7.4). As a result, base flow is diminished (Figure 7.3A, open bars). Because soils are very dry in summer and absorb much of the precipitation, storm flows are also reduced compared to cooler months with less insolation, plant activity, and ET (Figure 7.3A, vertically striped bars).

Long-term mean stream discharge for the Choptank River and Birch Branch in the drainage basin of the coastal lagoons (Figure 7.1) exhibits a similar seasonal pattern. Each has a maximum in spring and a minimum in late summer or early fall (Figure 7.3B), which is consistent with the groundwater levels observed regionally (Figure 7.4). However, the Choptank has later spring discharge and recharges more slowly in the fall (Figure 7.3B), an effect of the more poorly drained soils in the gauged basin of the Choptank, which lies largely in the poorly drained uplands of the Delmarva Peninsula (Lee et al. 2001). Under very dry conditions (e.g., summer of 2007), surface discharges from the coastal lagoon drainages such as Birch Branch virtually dry up due to the small watershed area and moderately well-drained soils (Beckert et al., in review). The stream beds become a series of interconnected ponds with little flow between them, although it is likely that groundwater flow continues below the surface. au: possible to update citation now?

At shorter time scales, moderately sized rain storms induce discharge events of 2- to 4-day durations (Figure 7.5A). Koskelo (2008) separated base flow (groundwater-based discharge) from storm flow (event-based discharge) in six Choptank watersheds using a new approach incorporating discharge patterns and rainfall (Koskelo et al., in review). Using this approach, base flow was found to be significantly and inversely related to hydric soils in long-term data due to surface ponding and root zone retention of rainfall and subsequent ET (Koskelo 2008). Storm flow was not related to soil drainage properties, but increased significantly with average surface topographic slope of the watershed (Figure 7.5B).

au: possible to update citation now?

7.4.2 Water Quality Trends: Nontidal Monitoring Stations

Water quality at the USGS gauging station at Greensboro, Maryland, has been declining for many decades (Figure 7.1). In primarily base flow sampling, NO_3^- has been increasing since the 1960s when water quality monitoring began, and total N (TN) has also increased since 1975 (Figure 7.6A). NO_3^- in base flow represents about 70% of the TN and is primarily derived from application of fertilizers on agricultural fields, which passes to streams via groundwater (Hamilton et al. 1993). As a result, both annual average TN and NO_3^- in Choptank streams are strongly correlated with percent agriculture in their watersheds (Fisher et al. 2006b; Figure 7.8).

Annual average total P (TP) concentrations (primarily base flow) have also significantly increased since monitoring began in 1970 (Figure 7.6B). Whereas NO_3^- is the major component of TN, phosphate (PO_4^{3-}) is a smaller component of TP and has not increased significantly over time (Figure 7.6B). In both panels of Figure 7.6, which illustrates trends in N and P, the data for 1984 were excluded from the regressions because of a small number of samples in that water year which included a single storm sample with very high concentrations. Overall, the data in this figure indicate that base flow N and P concentrations in the gauged portion of the Choptank Basin (Figure 7.1) have been increasing for several decades. There is significant interannual variation in water discharge, but no significant trend; therefore, trends in N and P fluxes (concentrations × water discharge) are primarily determined by changes in concentrations.

Similar trends have been observed for base flow in other watersheds within the Choptank Basin. Sutton et al. (2009b) compared the concentrations at 15 Choptank CEAP watersheds dominated

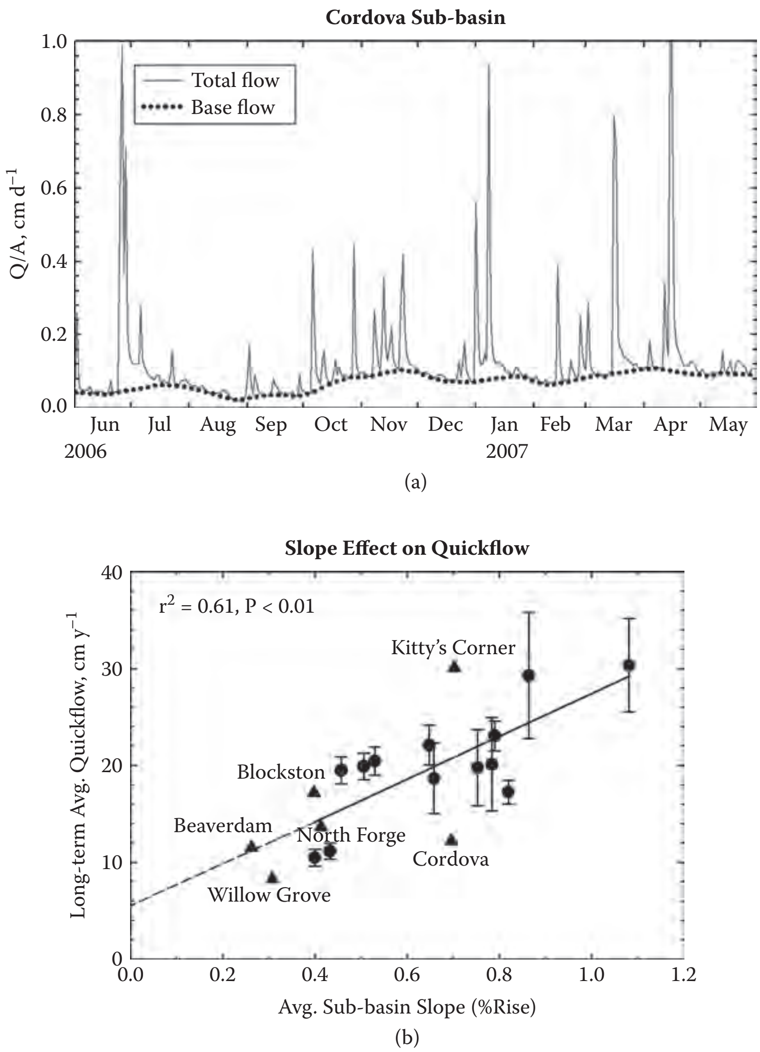


FIGURE 7.5 (a) Separation of quick flow and base flow in the Cordova watershed. (b) The effect of basin slope on the annual average volume of quickflow from storm events. Steeper average slopes in a watershed generate greater quickflow. Data from Koskelo (2008).

by agriculture (Figure 7.1). These watersheds were sampled in 1985 to 1986 and in 2003 to 2006 (Figure 7.7). While lacking the detailed time series available for Greensboro (Figure 7.6), the data for these watersheds (Figure 7.7) show no evidence of systematic decreases in base flow N or P concentrations between 1986 and 2003 to 2006 due to management actions within these watersheds. In fact, one watershed (Oakland) exhibited significant increases in TN and NO_3^- concentrations, similar to Greensboro (Figure 7.6).

One of the agriculturally dominated watersheds in the Choptank Basin shown in Figure 7.7 is the German (or Jarmin) Branch watershed, the site of the first targeted watershed program in Maryland during 1990 to 1996 (Primrose et al. 1997). Within this watershed there was nearly 100% application of the agricultural BMPs of soil conservation and water quality plans, nutrient management plans, and conservation tillage, with small increases in riparian buffers and winter cover crops. Continuous quantitative data on the management practices are not available except for 1990 to 1995, and fertilizer and manure applications and other agricultural practices probably

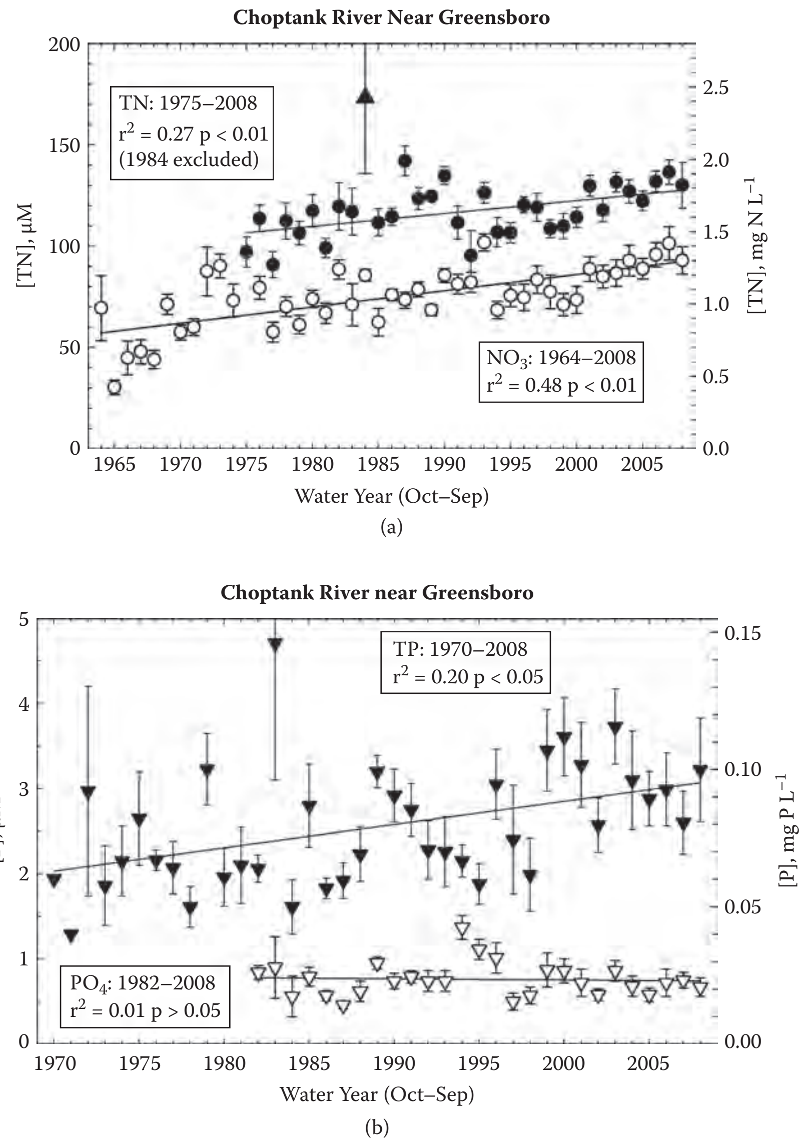


FIGURE 7.6 Changes in annual average concentrations of total N (TN), nitrate (NO_3^-), total P (TP), and phosphate (PO_4^{3-}) over the last 45 years at the USGS gauging station on the Choptank River near Greensboro, Maryland (01491000). Data from USGS.

varied during 1996 to 2006. With this caveat, 10 years after the targeted watershed project (more than the median groundwater residence time of 8 years in this basin), there were no significant changes in base flow N during this 10-year interval (Sutton et al. 2009a). However, base flow N concentrations at German Branch did not increase, unlike the Choptank River at Greensboro (Figure 7.6A). Furthermore, TP in base flow at German Branch decreased significantly (~50%), again in contrast with increasing P at Greensboro (Figure 7.6B). P is difficult to sample quantitatively because it increases dramatically during short-term storm events with large discharges (Fisher et al. 2006b). More than 80% of the annual P export from Choptank watersheds occurs during brief storm events (Koskelo 2008), making base flow measurements of P unrepresentative of annual export. Furthermore, storm flow is rarely sampled adequately in monitoring programs,

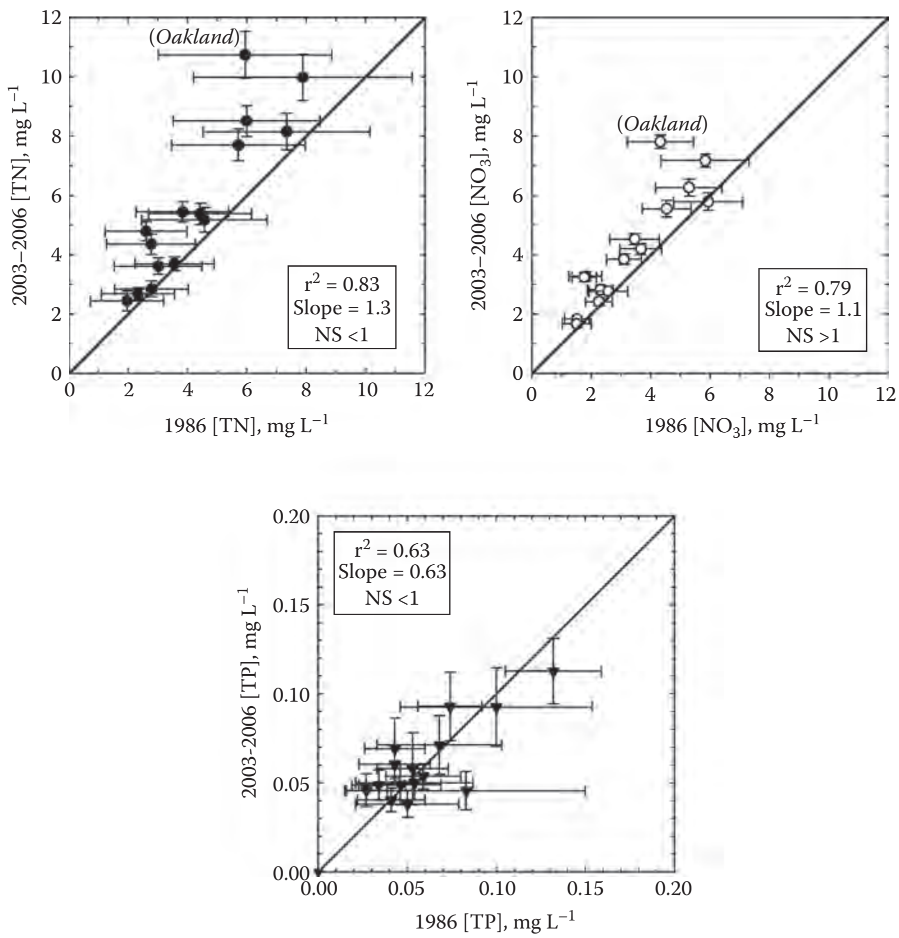


FIGURE 7.7 Comparison of multi-year averages of N and P concentrations in stream waters (base flow) of 15 agriculturally dominated watersheds in the Choptank Basin. Overall, there were no significant changes between the two time periods (all slopes not significantly different from 1). However, total N (TN) and nitrate (NO_3^-) increased significantly in base flow of the Oakland watershed (see Table 7.1). Data from Sutton et al. (2009a).

and the data in Figures 7.6 and 7.7 are essentially base flow data. Nevertheless, the stable N concentrations and decreasing P concentrations in base flow at the German Branch watershed compared to the continuous increases at Greensboro (Figure 7.6) indicate that intensive management in a targeted watershed program can have a detectable effect. Since changes in base flow chemistry were relatively small, insufficient applications of effective practices (winter cover crops, stream buffers) or relatively ineffective management actions (nutrient management plans, which are not monitored, nor have they ever been tested) resulted in small water quality effects detectable only after a decade of time.

7.4.3 Water Quality Drivers of Change

There are two major drivers of the poor water quality trends reported above (i.e., agriculture and sewage disposal). Agricultural lands are the primary driver of water quality in nontidal streams of the Choptank Basin and the Delmarva coastal bays due to application of fertilizers and distribution of manure from animal feeding operations (Figure 7.8). As a result, nontidal streams in coastal

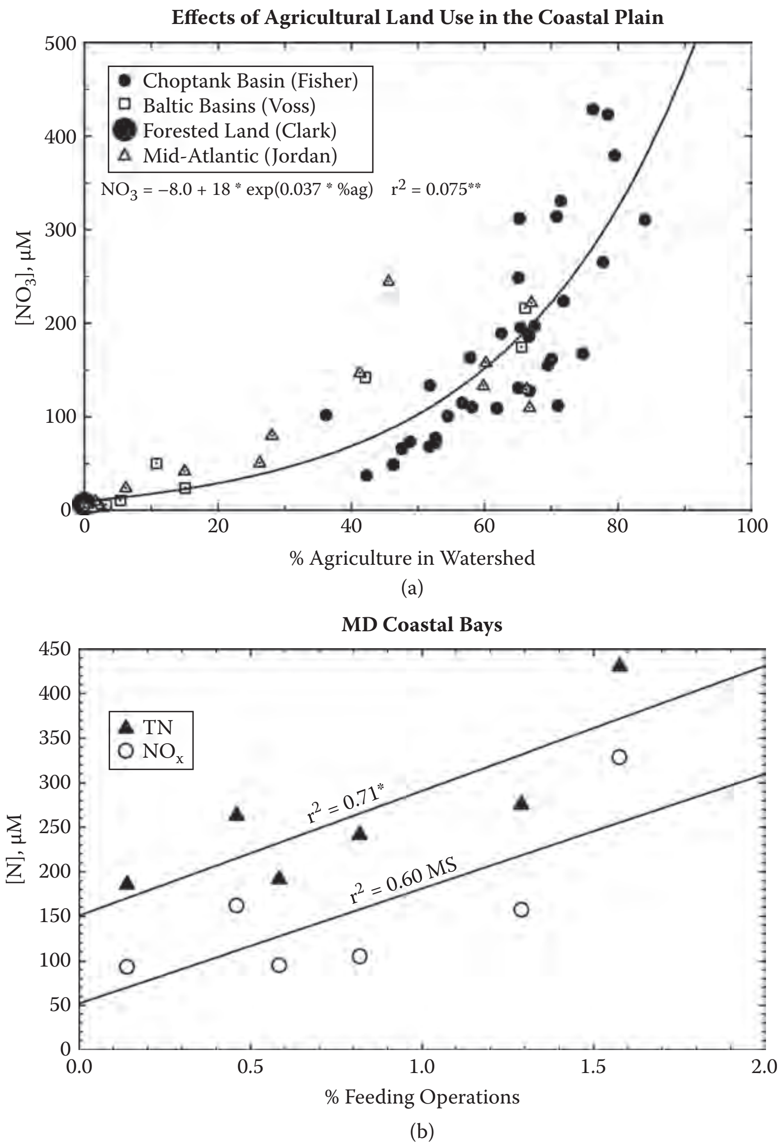


FIGURE 7.8 (a) Effects of percent agriculture (cropland) on nitrate concentrations [NO_3^-] in coastal plain watersheds. The exponential curve was forced through the extensive summary by Clark et al. (2000) on forested lands (= 0% agriculture). (b) Effects of animal feeding operations on average stream N in the St. Martin Basin in the Maryland coastal bays (Beckert 2008). The correlation with TN is significant, whereas the nitrate correlation is marginally significant ($p = 0.07$ and not significant for ammonium ($p > 0.10$).

plain areas, including Delmarva, carry large quantities of agricultural NO_3^- (Figure 7.8A), and the relationship between NO_3^- concentration and percent agriculture is nonlinear due to the substitution of croplands for landscape sinks for NO_3^- such as riparian forests and wetlands as the percent agricultural land use increases beyond 50%. Loss of the remaining wetland and riparian sites results in both new agricultural source areas for NO_3^- and losses of denitrifying areas, accelerating the increase of NO_3^- with additional agricultural land use. In the Maryland coastal bays (St. Martin Basin, Figure 7.8B), the percent land use of animal feeding operations, the area covered by the footprint of chicken houses within each watershed, was the most important determinant of TN and NO_3

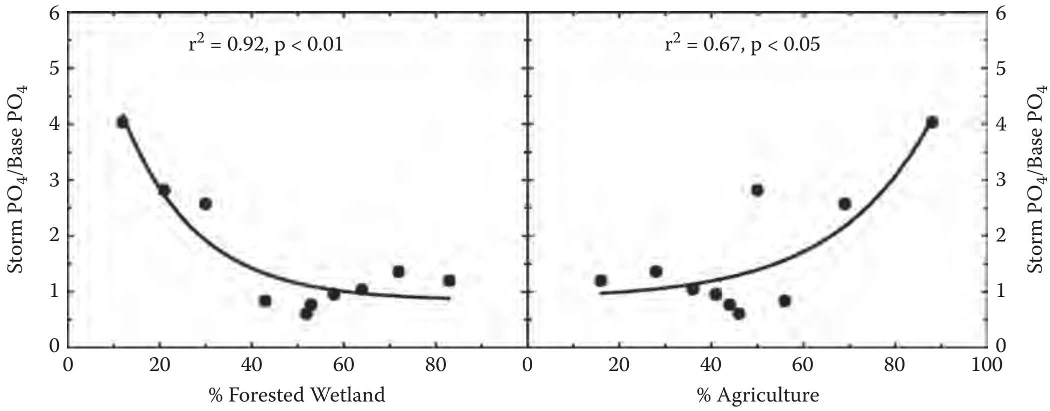


FIGURE 7.9 The ratio of storm phosphate (PO_4^{3-}) and base flow PO_4^{3-} in streams of the Little Blackwater Basin, just south of the Choptank Basin (Figure 7.1). In watersheds with >20% forested wetlands, there was no change in PO_4 between base flow and storm flow (storm PO_4^{3-}/base PO_4^{3-} = 1); however, as the forested wetlands decreased to <20% and percent agriculture increased beyond 50% land use, the amount of PO_4^{3-} in storm flow rose to four times the base flow value. Data from Stone et al. (in review).

au: please update

concentrations in nontidal streams. Despite the small area of the actual structure for the feeding operation, the distribution of manure from the houses to nearby fields has a significant impact on N concentrations in streams. A similar significant relationship between base flow PO_4 levels and density of chicken houses (number per km^{-2}) was also found among the Choptank CEAP watersheds ($r^2 = 0.47$, $p < 0.01$; Koskelo 2008).

Land use effects on P concentrations in streams are more difficult to quantify. As described above, most P is mobilized from watersheds during storms, which are usually vastly under-sampled in watershed studies (Koskelo 2008). However, Stone et al. (in review) has documented land use effects on N and P in both storm and base flows in the Little Blackwater watershed (Figure 7.9), which lies just south of the Choptank Basin (Figure 7.1). In this example from 2005 (Figure 7.9), PO_4^{3-} concentrations in storm flows were up to four times higher than in base flows from areas dominated by agriculture; in contrast, areas dominated by forested wetlands showed no such enhancement of PO_4 in storm flows. Fisher et al. (2006b), Sutton (2006), and Koskelo (2008) also showed P enhancement in storm flows >10 times higher than base flow concentrations in agriculturally dominated watersheds of the upper Choptank Basin.

au: possible to update Stone et al.?

Wastewater discharge is the second major driver of poor water quality. There are 10 wastewater treatment plants in the Choptank Basin, which discharge an average of 4.0 kg N and 1.2 kg P person^{-1} yr^{-1} primarily to tidal, estuarine waters (Figure 7.10). While the inputs of wastewater N are a small fraction (4%) of the Choptank nutrient budget due to the importance of agricultural nitrate (Figure 7.8), wastewater P is a large fraction (49%) of the P budget (Lee et al. 2001). The Choptank Basin has been slowly urbanizing (Benitez 2002), which has resulted in increases in the size of the small towns, the service populations, and wastewater N and P inputs to the estuary. Additions of tertiary treatment at several of the larger plants since 1990 have decreased N and P concentrations in some discharges, but larger wastewater volumes from increasing service populations have offset the effect on fluxes (Fisher, unpublished).

7.4.4 Agricultural N and P Reduction

Due to the importance of agriculture in determining stream N concentrations (Figure 7.8), many BMPs have been implemented in the Choptank Basin to reduce N and P losses from croplands. The BMPs include: (1) nutrient management plans; (2) conservation tillage; (3) drainage control

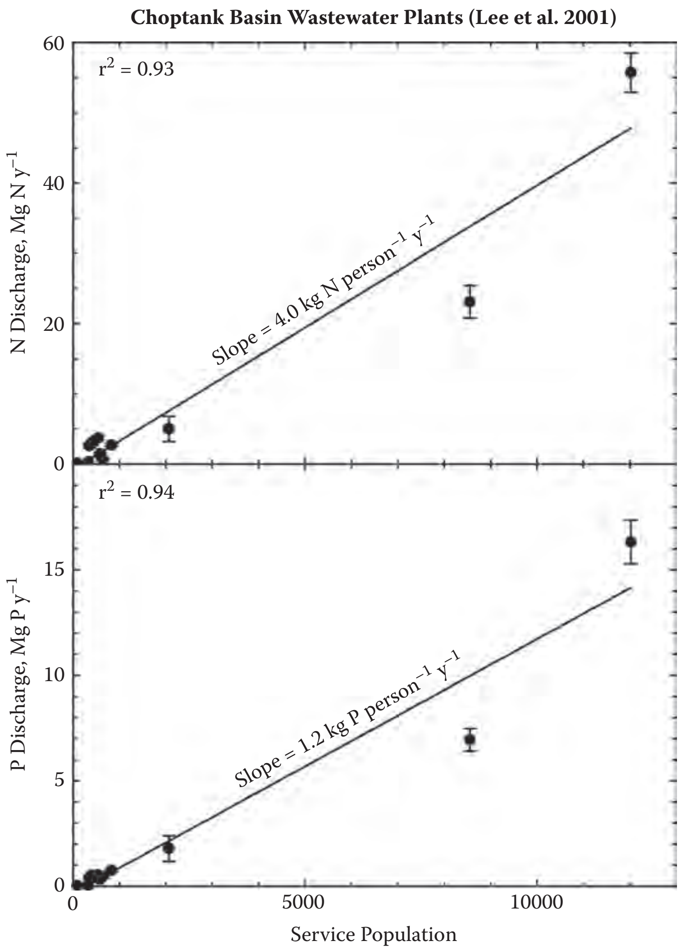


FIGURE 7.10 Total N and Total P discharge by the 10 NPDES wastewater treatment plants in the Choptank Basin. As the population serviced by the plants increases, discharges of N and P increase by approximately 4.0 kg N and 1.2 kg P person^{-1} yr^{-1}.

structures; (4) grassed or forested stream buffers (e. g., Conservation Reserve Enhancement Program or CREP); and (5) winter cover crops (Staver and Brinsfield 1998). Nutrient management plans are documents submitted by farmers to Maryland Department of Agriculture providing details on how their farming operations will avoid nutrient losses to surface water and groundwater. Conservation tillage is the use of herbicides to control weeds in place of plowing to avoid soil disturbance and reduce soil erosion. Drainage control structures are weir-like devices used to control water levels in cropland drainage ditches originally dug to improve the drainage of wet areas. Stream buffers are vegetated areas that border flowing surface waters (seasonally mowed grasses or managed forests) in which no fertilization takes place, but denitrification, plant uptake of N and P, and particle trapping do occur. Winter cover crops are cold-season grasses, such as rye or winter wheat, which stabilize the soil, reduce erosion, and provide N and P uptake during the fall through spring seasons. The function of these BMPs is (1) to physically trap soil and P during overland flow events (conservation tillage, cover crops, buffers); (2) to induce cool season plant N uptake to reduce nitrate leaching to groundwater during infiltration events (cover crops); and (3) to encourage denitrification, primarily in groundwater as it flows through a C-rich and O_2-poor environment (drainage structures, buffers). Lowrance et al. (1997) has reviewed riparian buffers in the Chesapeake region.

The concept behind nutrient management plans is to consider the nonpoint source nutrient contributions of individual farms. These plans have six components involving disposal and storage of manure, field management to reduce nutrient losses, and farm management documentation. In the plan, farmers are asked to demonstrate attempts to minimize environmental effects of livestock and row crop agriculture, and annual plans are now mandatory in the state of Maryland. However, the effectiveness of these plans has never been demonstrated at any scale, and there is no monitoring to validate whether plans are being followed.

Conservation tillage has two components ("low till" and "no-till"). Both substitute varying amounts of herbicide control of weeds for mechanical tillage, and the major goals are to reduce energy costs, stabilize soils, and reduce soil erosion. In a paired watershed study, Staver et al. (1994) showed that soil erosion was significantly less in the watershed with conservation tillage compared to the watershed with conventional tillage. However, despite the reduced soil erosion in the watershed with conservation tillage, leaching and transport of crop P increased during overland flows because of the P-rich crop litter concentrated at the soil surface. Therefore, conservation tillage appears to reduce soil erosion while increasing P losses from crop fields.

Drainage control structures are being experimentally applied to farm ditches originally cut through wetlands to enable adequate drainage for conversion to agriculture. The soils are usually hydric (poorly drained, with high water content during the cool season), and the drainage ditches often export water with millimolar concentrations of NO_3^- (700 to 1000 μM or 10 to 15 mg NO_3^--N L^{-1}) from the adjacent agricultural fields. This value is consistent with the extrapolated right y intercept (720 μM or 10.1 mg NO_3^--N L^{-1}) for the regression line at 100% agriculture in Figure 7.8A. Drainage control structures are used to raise the water levels close to the root zone both to store water in groundwater for summer crop use as well as to induce denitrification in C-rich upper soil horizons.

We have strong evidence of denitrification in groundwater entering a drainage controlled ditch (Figure 7.11). In this example from the flooded section of the ditch above the drainage control structure, excess N_2-N accumulated in groundwater near the ditch at concentrations of 200 to 400 μM above that of atmospheric N_2-N equilibrium (~1200 μM). NO_3^- shows strong seasonal variations, varying from 0 to 700 μM with groundwater levels. During winter and spring, when groundwater levels are highest, NO_3^- is typically 400 to 700 μM; during late summer and fall, when groundwater gradients relax (Figure 7.4), NO_3^- is much lower (0 to 200 μM). A particularly dry summer in 2007 caused low groundwater levels and low concentrations of NO_3^-, which did not recover until March 2008. Note that less excess N_2-N accumulated in groundwater (~350 μM) than the net disappearance of NO_3^- (~700 μM). This appears to result from diffusive loss of excess N_2-N from the supersaturated groundwater into the vadose zone above and ultimately to the atmosphere (Fox et al. 2009). In contrast with the flooded section of the ditch upstream of the drainage control structure, the unflooded control section of the ditch downstream of the drainage control structure had groundwater NO_3^- levels continuously >1000 μM, and excess N_2-N was <100 μM, with little seasonal variation (data not shown).

Other gases also accumulate in groundwater associated with the flooded section of the ditch. Nitrous oxide-N (N_2O-N) is a by-product of both denitrification and nitrification (Wrage et al. 2001), and in the example in Figure 7.11, N_2O accumulates up to 6 μM, considerably higher than the atmospheric background of 0.02 nM. Both here and in other datasets (R. Fox, unpublished), N_2O-N typically accumulates to 0.5% to 5% of the excess N_2-N. Methane (CH_4) also accumulates in groundwater when NO_3^- decreases to <100 μM (Figure 7.11). Very high concentrations of CH_4 typically occur at the end of summer when water levels (Figure 7.4), hydrostatic head, and NO_3^- are low. These high accumulations of CH_4 may lead to brief ebullition (degassing) events in which gases dissolved in groundwater are partially removed by CH_4 bubble formation (August 2007 in Figure 7.11).

The drainage control structure improved water quality in surface waters (Figure 7.12). When we first began sampling the ditch waters in 2006 (about one year after the installation of the drainage

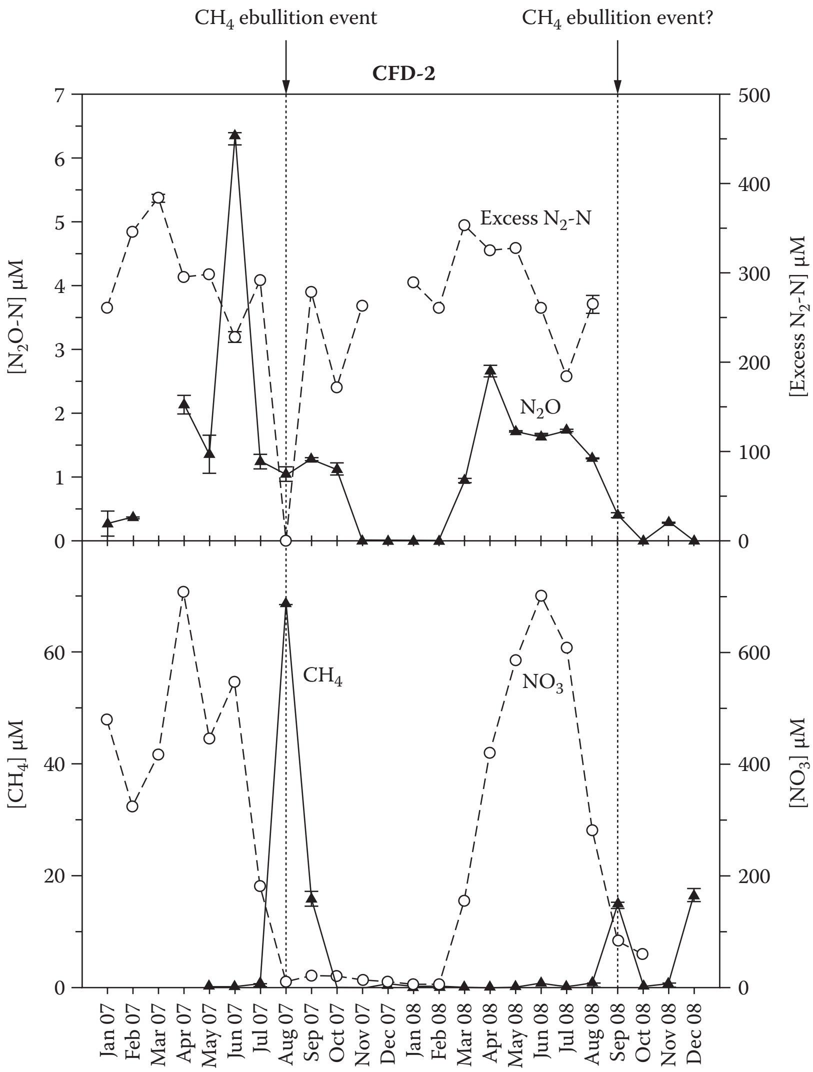


FIGURE 7.11 An example of a time series of concentrations of nitrate (NO_3^-) and the metabolic dissolved gases nitrous oxide (N_2O), methane (CH_4), and excess N_2-N dissolved in shallow groundwaters in the Choptank Basin. Excess N_2-N routinely accumulated in groundwater up to 25% to 50% of atmospheric N_2-N (~1200 µM at 12°C) as NO_3^- was denitrified as an alternate electron acceptor within the soil matrix under suboxic conditions (8% to 15% saturation, not shown). N_2O-N also accumulated to 1–10 µM (~20,000 times the atmospheric background of ~0.02 nM) and was typically 0.5% to 5% of the excess N_2-N. CH_4 accumulated when NO_3^- was depleted and CO_2 became the terminal, alternative electron acceptor. Accumulations of CH_4 > ~50 µM (~20,000 times the atmospheric background of 2 nM) resulted in ebullition events (bubble formation) which stripped out other dissolved gases (August 2007).

control structure), there was a large contrast between surface water in the upper, flooded section of the ditch (NO_3^- = 0 to 200 µM) and the lower unflooded section of the ditch (NO_3^- = 500 to 1200 µM). However, it is clear that over time, NO_3^- in the unflooded section of the ditch has decreased, either as a result of the very dry year 2007 or as a result of NO_3^--depleted groundwater from the upper perched section bypassing the drainage control structure. Regardless of the cause of the NO_3^- decrease in the unflooded section downstream of the control structure, it is clear that the

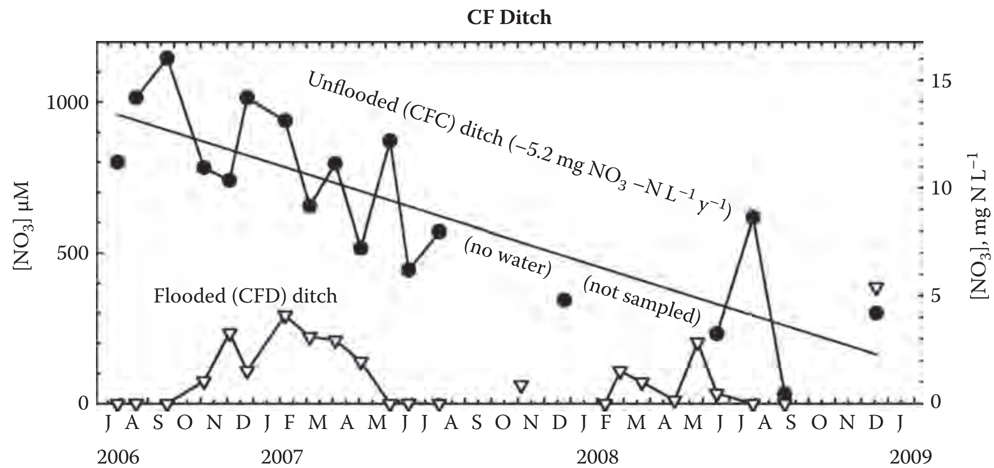


FIGURE 7.12 Chronology of NO_3^- concentrations in surface water of a 1-km long farm ditch divided in half by a drainage control structure. The upper, flooded section has raised groundwater levels to within ~1 m of the soil surface, whereas in the lower, unflooded section the groundwater levels are ~2 m below the soil surface.

drainage control structure has a large impact on agricultural NO_3^- discharged in upstream surface waters, allowing significant NO_3^- to pass only during the cool season (Figure 7.12) when temperatures are lower and hydrologic gradients are greater (Figure 7.4). However, this BMP is still experimental and has not yet been widely applied in the Choptank.

Strong land cover effects on the concentrations of dissolved gases are observed in groundwater (Figure 7.13). CH_4 concentrations are highest (average = 23 ± 13 μM) at wetland sites, followed by wet areas close to wetlands (average = 4 ± 2 μM) due to low or depleted O_2 and NO_3^- as electron acceptors for respiration. CH_4 is lowest under farm fields, grassed CREP buffers, and forests (<1 μM) due to the presence of significant amounts of O_2 and/or NO_3^-. Similarly, N_2O is highest in wetlands (average = 0.8 ± 0.4 μM) and CREP buffers (average = 0.6 ± 0.4 μM) due to denitrification of NO_3^- from adjacent agricultural fields, and N_2O is lowest in wet areas, farm fields, and forests (<0.4 μM) due to apparent reduction (denitrification) of N_2O (wet areas) or the presence of O_2 (farm fields and forests).

Another BMP implemented in the Choptank Basin to reduce losses of agricultural N and P is restoration of stream buffers. These areas were originally cleared for agriculture where slopes were low or where topography was altered, primarily on first- or second-order, nontidal streams on farms. The CREP program of USDA now makes funds available to farmers to reforest or plant grasses on these streamside areas to reduce transport of agricultural N and P from crop fields to streams.

Restoration of forested stream buffers has been quantified for the agriculturally dominated Choptank watersheds listed in Table 7.1 by Sutton et al. (2009b). During 1998 to 2005, 11% of streamside vegetation (range 1% to 30% within each watershed) was replanted under USDA's CREP Program, increasing the preexisting forested buffers (average = 33%, range = 10% to 48%). Streamside lengths were defined as 2 × stream lengths within each watershed. In 2005 total buffered streamsides (preexisting + CREP) averaged 44% (range = 12% to 61%) within the watersheds. Multi-year water quality data were used to examine the effect of the 11% average increase in streamside vegetation resulting from the CREP program, but no significant effects were detectable. Concentrations of N and P in streams of these watersheds have not changed or have slightly increased in some streams over the previous 20 years (Figure 7.7). Sutton et al. (2009b) attributed the lack of a statistically detectable effect to (1) the young age of the buffers resulting in low plant uptake and denitrification; (2) possible increases in agricultural N and P loading (e.g., increased

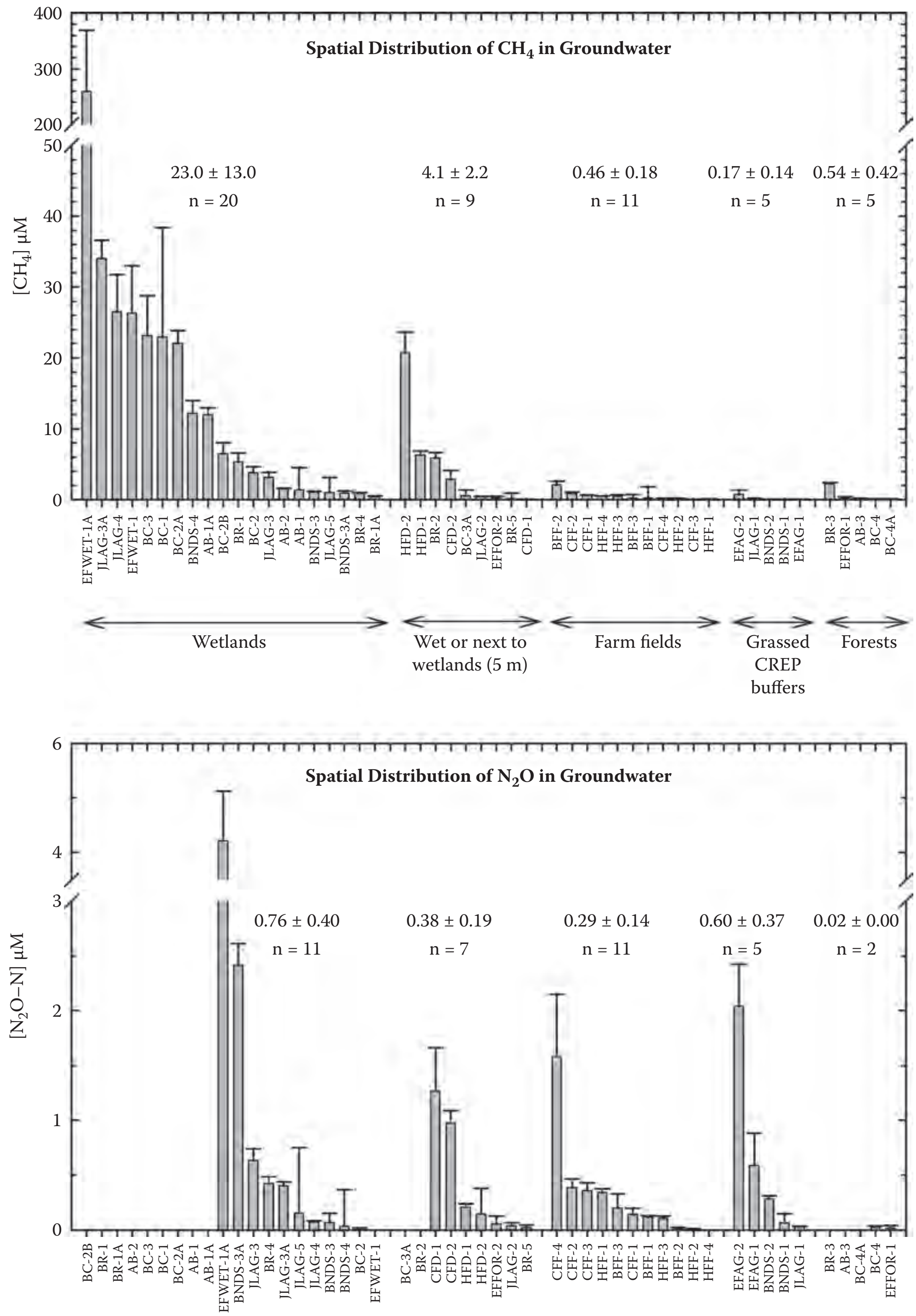


FIGURE 7.13 Spatial distributions of methane (CH_4) and nitrous oxide (N_2O-N) dissolved in groundwater in the Choptank Basin. Groundwater piezometers are grouped in classes (wetlands, wet areas, crop fields, buffers, forests) and sorted by the average (±SE) of 2008 data (12 monthly observations). Wetlands and wet areas have the highest CH_4 due to a lack of or depleted NO_3^-, whereas all classes except forest have high N_2O due to production during both nitrification and denitrification.

fertilizers or manure applications, double cropping, etc.); and/or (3) insufficient implementation of buffers (33% preexisting to 44% preexisting + CREP). Bypassing of buffers by deeper groundwater flow paths (see Lowrance et al. 1997) is another possible explanation for the lack of a significant effect.

The use of winter cover crops is the last BMP implemented in the Choptank Basin to reduce losses of agricultural N. Planting of these winter annual grasses as soon as possible after crop harvest has been shown to stabilize soil (reducing erosion and P losses) and create demand for N in soils after N mineralization and oxidation produce highly soluble NO_3^- (Staver and Brinsfield 1998; Staver 2001a). Under low evapotranspiration rates in winter, rainfall produces large infiltration events which replenish groundwater levels (Figure 7.4) and transports soil NO_3^- to the groundwater (Staver and Brinsfield 1998; Staver 2001a). Larger rainstorms also generate overland flow which transports soil P rapidly to streams (e.g., Figure 7.9; Fisher et al. 2006b). The presence of cover crops acts to immobilize N and P during the winter in organic forms, making these available to crops during the following growing season. Field-scale tests of winter cover crops have been shown to reduce fluxes of both N and P (Staver and Brinsfield 1998), but the aggregate effects of winter cover crops has not been adequately tested at the watershed scale. In German Branch watershed (described above), Sutton et al. (2009a) found no significant changes in base flow N and decreases in base flow P after widespread application of BMPs, including winter cover crops. However, winter cover crops were one of several BMPs, and only 0% to 4% of crop fields in the German Branch watershed had winter cover crops.

7.4.5 Estuarine Water Quality Conditions

During 23 years of water quality monitoring at station ET5.2 in the Choptank Estuary (Figure 7.1), there has been no discernable improvements in water quality (Figure 7.14). Annual average values of chlorophyll-*a* have increased, with a relatively large interannual variability driven primarily by variations in annual river discharge (positive relationship, $r^2 = 0.57$, $p < 0.01$). Likewise, there has been a decrease in summer bottom dissolved oxygen concentrations; however, these are not significantly related to river discharge but are negatively correlated with annual average chlorophyll-*a* in surface waters ($r^2 = 0.47$, $p < 0.01$), the source of the sedimenting organic matter that results in strong biological oxygen demand in bottom waters.

Projections for water quality over the next decade are worrisome (Figure 7.14). Linear extrapolation of the trend in the upper panel to 2015 predicts annual average chlorophyll-*a* >20 μg L^{-1}, a threshold often associated with increased bloom frequency (U.S. Environmental Protection Agency 2007). Likewise, linear extrapolation of the trend in the lower panel indicates that the average summer bottom dissolved oxygen will be approaching the EPA Bay Program's 30-d water quality criterion (3 mg L^{-1}). Negative excursions in wetter years with higher chlorophyll-*a* are likely to result in average summer dissolved oxygen less than the 2 mg L^{-1}, causing severe biological impacts. These conditions are not limited to the Choptank Estuary or the Chesapeake Bay, and Wazniak et al. (2004) and Beckert (2008) have reported similar conditions in the Maryland coastal bays, particularly in summer tidal waters at the northerly, more populated end of these systems.

7.5 DISCUSSION

Most agricultural and urban BMPs applied nationally have not been tested quantitatively for effectiveness at the watershed scale (Bernhardt et al. 2005). Despite national programs encouraging various economic and agricultural policies (e.g., nutrient management plans, CREP, winter cover crops, etc.), little is known about time scales of watershed responses or incremental reductions in export of N or P expected for application of BMPs at the watershed scale. The examples of our research given above strongly support the need for quantitative evaluation of BMPs to establish time scales of response as well as the expected decrease in N or P concentrations per unit BMP applied at the

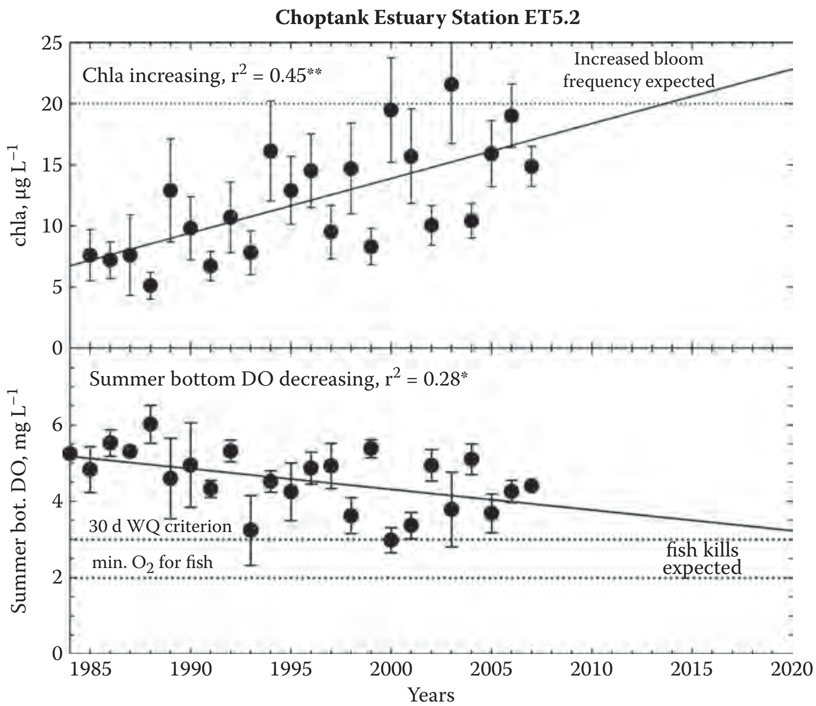


FIGURE 7.14 Trends in annual average values of chlorophyll-*a* (chl*a*) concentrations in surface waters and summer (June to August) dissolved O_2 in bottom waters of the Choptank Estuary at EPA Bay Program station ET5.2 (see Figure 7.1 for location). There have been significant changes in both of these water quality parameters, and projections of the trends into the next decade suggest increased algal blooms in surface waters as annual average chl*a* increases beyond 20 µg L^{-1} and fish kills in bottom waters as the normal range of dissolved O_2 results in summers with <2 mg O_2 L^{-1}.

watershed scale. Examples of adequate tests are longitudinal studies in one watershed (e.g., Sutton et al. 2009a, for the German Branch watershed) or parallel studies in multiple watersheds with similar amounts of agriculture but varying amounts of a single BMP (e.g., Sutton et al. 2009b). Our strongest research recommendation is for more testing of BMPs at the watershed scale to provide quantitative information on response time and reductions of N and P per unit BMP applied.

7.5.1 Water Quality Status

It is clear that water quality in the Choptank Estuary is approaching a threshold. Driven by nutrient inputs from the terrestrial basin, projections of current trends in the estuary suggest algal blooms in surface waters and losses of benthos and fish from bottom waters in the coming decade. Most indicators of watershed nutrient inputs from the two largest sources, agriculture (Figures 7.6 to 7.8) and sewage (Figure 7.10) indicate that no significant reductions and some increases have occurred in the last 40 years (Figures 7.6 and 7.7). Given the relative stability of agricultural land use (Benitez and Fisher, in review) and increases in human populations (Fisher et al. 2006a), there is little hope for improved water quality in the estuary under current conditions and policies.

au: possible to update Benitez and Fisher citation?

There are four primary reasons for the lack of progress in water quality in the Choptank Estuary and elsewhere: (1) the voluntary approach taken by the EPA Bay Program to improve water quality; (2) insufficient implementation and watershed-scale testing of BMPs; (3) time lags for water quality improvements to appear; and (4) strong economic incentives to continue business as usual without regard to environmental consequences. Each of these reasons is discussed below, and in the next section, we present a summary of suggested changes to counteract these reasons for the lack of progress in improvements in water quality.

The single largest problem in the Chesapeake Bay watershed is excess N and P entering the bay from land (U.S. Environmental Protection Agency 2007). However, despite this, the EPA Bay Program has taken a largely voluntary approach, encouraging farmers and homeowners to reduce their use of fertilizers, with no oversight or enforcement. However, there are relatively few incentives to reduce nutrient losses. Farmers have strong economic incentives to continue to maximize crop yields to get the largest net income by applying fertilizers or manures, and Figure 7.8 provides strong evidence that excess agricultural fertilizers and manure are the primary drivers of N concentrations in Delmarva streams. Vitousek et al. (2009) show an average of +10 kg ha^{-1} yr^{-1} surplus of agricultural inputs of N (155 kg ha^{-1} yr^{-1}) over outputs (145 kg ha^{-1} yr^{-1}) in the U.S. Midwest, although it may be the outliers at the high end of input distributions embedded within a watershed that drive patterns such as those shown in Figure 7.8. Similarly, homeowners are given advice by the Cooperative Extension Service and other sources to apply lawn fertilizers at a rate of 87 to 174 lbs N $acre^{-1}$ yr^{-1} (equivalent to 99–195 kg N ha^{-1} yr^{-1}, see http://agbiopubs.sdstate.edu/articles/ExEx1016.pdf, accessed August 25, 2009). This rate is equivalent to N applications for corn (100 to 150 lbs N $acre^{-1}$ yr^{-1} or 110 to 170 kg N ha^{-1} yr^{-1}), one of the most heavily fertilized crops in the Choptank Basin. In a study of turf in New England, Guillard and Kopp (2004) used four fertilizer types applied at a rate of 147 kg ha^{-1} yr^{-1}, in the range given above, and found volume-weighted mean NO_3^- concentrations in leachate from inorganic fertilizers of 5 mg N L^{-1}, in the mid-range of average stream NO_3^- in agriculturally dominated basins in Figure 7.7. Fertilized lawns can potentially make a large, distributed, and heterogeneous contribution to high groundwater nitrate which becomes base flow nitrate in streams. However, the distribution of fertilized lawns is poorly known, making a quantitative assessment problematic. Nonetheless, in a nutrient overloaded system, reducing fertilizers applied for aesthetic reasons should take place before fertilizer reductions on crop fields used for food production.

The second reason for lack of progress in water quality in the Choptank Basin is insufficient implementation and watershed-scale testing of BMPs. In the targeted watershed study in German Branch referred to above (Primrose et al. 1997), nearly 100% compliance with some BMPs was achieved (e.g., nutrient management plans, conservation tillage); however, these have not, to our knowledge, ever been tested individually at the watershed scale to quantify their effectiveness. Sutton et al. (2009a) evaluated the collective effectiveness of all applied BMPs; however, the water quality effect was small, and it was impossible to attribute the observed effects to individual BMPs. Furthermore, newer and more promising BMPs such as winter cover crops, were only lightly used (0% to 4%), and even the CREP program funded by USDA to restore streamside vegetation increased the average stream buffer coverage only from 33% to 44% in 15 agriculturally dominated watersheds in the Choptank Basin (Sutton et al. 2009b). On average, more than half of all first- and second-order streams in the Choptank Basin had no buffers in 2005. More extensive implementation would provide a stronger water quality signal to detect, and more rigorous testing of individual BMPs at the watershed scale would provide a rational and quantitative basis for expectations of water quality improvements following implementation.

The third reason for a lack of progress towards improved stream water quality is time lags associated with groundwater emergence. Groundwater residence times in the unconfined surface aquifer are typically years to decades (Winter 1983; Staver 2001b), and some water quality improvements in groundwater may have already been achieved; however, there is less systematic monitoring of groundwater compared to streams, and groundwater time lags may obscure the effects of BMPs influencing groundwater chemistry. Even in our study of the controlled drainage structure described above (Figure 7.12), several years were required until the effects of the raised water table on water quality in a first-order stream (the ditch) were observed. We may yet detect more effects of some current BMPs in surface waters over the coming decade as younger, potentially cleaner groundwaters reach surface waters, but continued monitoring will be required to quantify these effects.

The final reason for the lack of progress in nontidal water quality is the lack of economic incentives for improved water quality. Currently, economic incentives favor a "business-as-usual" approach in the absence of regulations or enforcement, and high export rates of N and P are expected from land to water under these conditions. Neither farmers nor land owners are penalized for over-applying fertilizers (other than the cost of the fertilizer), and there are no economic incentives for improved environmental conditions or disincentives for environmental degradation. Only point sources have been systematically regulated in response to increases in human populations that provide wastewater. In the long term, economic incentives due to avoidance of areas with poor water quality may provide some pressure to solve these problems, but current prospects are dim, except for pressure from a small fraction of the population active in local water quality issues.

7.5.2 Water Quality Improvement

We have used the data presented here to develop a series of policy recommendations which could potentially provide a rational basis for improvements in water quality. These include (1) applications of water quality standards in nontidal watersheds; (2) lower caps on wastewater discharge volume and concentrations; (3) lower fertilizer application rates on farms (subsidized); (4) buffers and cover crops on crop fields; and (5) limited applications of lawn fertilizers. All of these recommendations are described below, and we emphasize that they are based on our own observations. More detailed policy considerations by government agencies (e.g., US EPA, USDA NRCS, MD DNR, MDE, etc.) will be required to place them into practice.

The first recommendation for improving water quality on Delmarva is the implementation of numeric water quality standards for nutrients in nontidal waters at the watershed scale. The US EPA (2000) has proposed water quality standards for nutrients in nontidal waters, but to our knowledge these standards have neither been adopted nor applied in the Mid-Atlantic region or elsewhere. US EPA (2000) recommended 0.71 mg N L^{-1} (51 µM) and 0.031 mg P L^{-1} (1 µM) for the nutrient ecoregion XIV, which includes Delmarva. These water quality standards are equivalent to ~5 times the concentrations found in local nontidal streams draining forested areas and are much lower than observed concentrations in most agriculturally dominated basins in the Choptank Basin (e.g., Figure 7.8) and elsewhere (Jordan et al. 1997; Beckert et al. in review). This indicates widespread regional violation of the recommended, but unenforced, water quality standards.

au: possible to update Beckert et al. citation?

The original goal of the EPA Bay Program was a 40% reduction of the 1985 N and P loads (e.g., Belval and Sprague 1999). From the monitoring data presented above, it is clear that this goal has not been achieved in the Choptank Basin, despite optimistic model predictions, and the trends are not even in the right direction. A further complication is the fact that the Greensboro watershed gauged by USGS (Figure 7.1, 18% of the basin) is not representative of the remaining ungauged portion of the Choptank Basin (Lee et al. 2001). The Greensboro watershed has significantly less agriculture, more forest, and more hydric soils than most of the basin, which results in relatively low N and P concentrations (Lee et al. 2001). Jurisdictionally, half of the Greensboro watershed also lies in the state of Delaware, which does not participate in the Maryland tributary strategy.

Attainment of the 40% reductions of the 1985 N and P loads would undoubtedly have large impacts on water quality in the Choptank nontidal streams and estuary. In about 1985, N concentrations ranged from 110 µM (1.3 mg L^{-1}) at the Greensboro watershed to 430 µM (6.0 mg L^{-1}) at the Oakland watershed (Figures 7.6 and 7.7). If the efforts of the EPA Bay Program had achieved 40% reductions in the Choptank, N concentrations would now range over 67 to 260 µM (0.9 to 3.6 mg L^{-1}), considerably lower than those currently observed for total N (Figures 7.6 and 7.7). Parallel computations for 40% P reductions would result in current P concentrations of 0.5 to 2.5 µM (0.02 to 0.08 mg L^{-1}), also lower than those currently observed for total P (Figures 7.6 and 7.7). We strongly support the original goals of the EPA Bay Program's 40% reductions, and the numbers estimated above could be used as local water quality standards for the Choptank Basin. Attainment of the stricter EPA water quality standards should remain a long-term but much more difficult goal to achieve in this nutrient-rich basin. Because water yields are relatively uniform regionally at monthly to annual time scales (Sutton et al. 2009b), concentrations could be substituted for nutrient loads in water quality standards to simplify management protocols.

Evaluation of violation of a water quality standard would require extensive water quality sampling. Quarterly base flow sampling of all HUC 12 or 14 nontidal watersheds for a year could be undertaken by an independent agent (e.g., USGS, a local university, or a private consulting company) to determine attainment or violation of N and P standards in base flow. Validation, certification, and standardization of sampling protocols and chemical analyses would be essential. N is easier to sample than P, but base flow P can provide an initial value for P status in nontidal streams. Incorporating storm flow sampling is desirable, especially for P, but probably too expensive for the widespread application suggested here. Following a year of monitoring, watersheds in violation of water quality standards should be required to adopt an appropriate mix of the BMPs described below, with quarterly monitoring at 5-year intervals to assess progress towards water quality standards. Selected research watersheds such as those in Table 7.1 or the NAWQA watersheds of USGS could be used for more detailed studies. To provide an economic incentive, failure to attain a water quality standard after BMP implementation within a watershed after a decade (close to median groundwater residence times) should result in economic consequences for those living and using land within the watershed. This approach is similar to the TMDL process of EPA, but would be focused on nontidal streams, with fixed deadlines for compliance with concentration standards developed locally.

The second recommendation for improving water quality on Delmarva is to lower caps on wastewater volumes and concentrations. To our knowledge, there are currently only loosely enforced caps for wastewater volumes and nutrient mass discharge from wastewater plants, even in areas such as the Choptank with degrading estuarine waters (Figure 7.14). The current strategy of many municipalities is to add tertiary treatment to reduce the N and P concentrations in order to accommodate urban growth and increased wastewater volumes. A better approach would be to add wastewater volume caps and to lower N and P mass caps for a tributary or region. This would force wastewater plants to find alternative uses for human wastewater, a valuable product that can be better used for production of compost (e.g., Milorganite), methane, irrigation, and fertilizer products, rather than discharging wastewater into our swimming and fishing waters. Similarly, denitrifying septic systems should be mandatory on all new construction, and existing septic systems should be retrofit within a 5- to 10-year time period.

The third recommendation for improving water quality on Delmarva is to lower fertilizer application rates on farms. Fertilizer applications are currently targeted to maximize crop yields under the best weather conditions, with little consideration for the environmental consequences of unused N and P when crop uptake of N and P is limited by droughts or floods. We suggest that farmers apply fertilizers at lower rates to match crop yields. However, N budgets of crop fields are poorly known, especially under varying weather conditions (Vitousek et al. 2009). The data of Figure 7.8 indicate that agricultural land is a significant source of N, but the magnitude and spatial extent of excess N applications on crop fields is not clear. We recommend the development of national GIS databases on watershed N budgets (HUC 12 or 14), including application rates and crop yields to provide a rational basis for better N and P use efficiency. Much of this information is already compiled, but not systematically at appropriate spatial scales in a watershed context, and usually without spatial reference except at the county level. This recommendation simply endorses better use of information already being collected by different agencies.

In a recently funded pilot project, some of the authors are testing an alternative approach to reduced fertilizer applications. Economic incentives are being offered to a small group of farmers in the Choptank Basin to maintain their soil P and NO_3^- concentrations low in the fall at the end of the growing season to reduce cold season losses of P in overland flow and NO_3^- in infiltrating rain water during fall and winter storms. Achieving low soil P and NO_3^- in the fall will require repeated applications of fertilizers and manures at the rate that they can be utilized by the crops rather than a small number of larger applications. The result should be reduced losses of N and P from better managed crop fields, an outcome that will be monitored.

The focus of most agricultural policies has been on the production of inexpensive food with maximum profits by the producer, usually from increased production in decreasing areas (Benitez 2002; Fisher et al. 2006a). However, we suggest that an additional consideration must be the reduction of the environmental impact of high-intensity agriculture (Figures 7.6 to 7.8). We support the continued economic viability of agriculture on Delmarva, but we are attempting to provide recommendations for policies that reduce the impact of agriculture on water quality (Figure 7.8). We also suggest that the deleterious water quality effects of corn-based ethanol production should be added to other problems, including the greater C storage of unfertilized grasslands harvested for biomass (Tilman et al. 2006), greater energy production per unit area for cellulosic biofuels (Cambell et al. 2009), and competition with crop production for arable land (Tilman et al. 2009).

The fourth recommendation for improving water quality on Delmarva is mandatory stream buffers, drainage control structures, and winter cover crops on at least 50% of agricultural fields. Priorities for the 50% could be set by crop type (e.g., corn) or by fertilizer application type or rate (poultry or sludge) with the highest N and P loss rates. Buffers will take land out of agricultural production, as many first-order or zero-order streams are found within farm fields or are farm ditches. Buffering these areas will segment many fields and remove land that is currently farmed. An alternative to buffers for ditches could be the drainage control structures described above. Given the apparent, initial success of drainage control structures in reducing NO_3^- losses from a farm ditch in a former wetland converted to cropland (Figure 7.12), mandatory water controls on similar ditches might also be a good recommendation after testing at the watershed scale. Likewise, mandating winter cover crops (or unfertilized commodity crops) will have economic costs for which farmers should continue to be compensated. Prior to implementation of this recommendation, testing of the assumptions and the previous field-scale measurements should be done at the watershed scale.

The last recommendation for improving water quality on Delmarva is to substantially limit the use of lawn fertilizers. Given that excess N and P is the single largest problem in Chesapeake Bay and most coastal waters, the high rates of fertilizer applications to lawns (see above) seems to have no justification. If we are going to ask farmers to sacrifice their highest yields in perfect weather in order to reduce the losses of N and P from their fields under less perfect weather conditions, then we should also be willing to have a less green turf in our yards for a common cause. However, we acknowledge that there has been little quantitative study of the effects of nutrient losses from lawns at the watershed scale. There are clearly large losses of N from fertilized turf (e.g., Gilliard and Kopp 2004), but the areal extent of fertilized lawns and the quantitative significance has yet to be rigorously determined at the watershed scale.

au: spelled Guilliard in references and earlier in text; which is correct?

Many of these recommendations may seem draconian or invasive. Enforcement of water quality standards and BMPs will conflict with individual property rights and established agricultural and municipal practices. However, our current high-intensity society generates large amounts of N and P in surface waters draining the land that we inhabit (Figures 7.6 to 7.8), with significant impacts on coastal and estuarine waters (Figure 7.14). If we want to have clean waters in which to swim and fish, we have to take at least some of the steps recommended above. The fluxes of N and P from land to water are well known and defined, and the production of our food and disposal of our wastes are the largest sources. We have a choice of leaving cleaner waters to future generations if we take the steps listed above, or we can leave a legacy of green waters with lifeless bottom conditions.

ACKNOWLEDGMENTS

The research on surface hydrology and chemistry has been supported by subcontracts to TRF and TEJ from funding provided by the USDA's CEAP program to Laura McConnell and Greg McCarty at the USDA ARS lab in Beltsville, Maryland. Funding on groundwater and denitrification was provided to TRF and TEJ by the USDA CSREES program. Partial funding for land use and GIS support was also provided to TRF by NASA's Land Cover Land Use Change Program (NEWS04-2-0000-0420). RJF and KAB were supported by graduate fellowships and teaching assistantships from the Horn Point Laboratory (UMCES). We thank Jim Hagy and an anonymous reviewer for substantial improvements in the original manuscript.

REFERENCES

Beckert, K. A. 2008. Watershed land use and nutrient dynamics in MD coastal bays USA. M.S. Thesis, University of Maryland, College Park.

au: update publication details if available.

Beckert, K. A., T. R. Fisher, J. M. O'Neil, R. V. Jesien. In review. Characterization and comparison of stream nutrients, land use, and loading patterns in Maryland coastal bay watersheds. *Estuar. Coastal Shelf Sci.*

Bell, W. H. 2000. Moving water. Report to the Chesapeake Bay Cabinet by Public Drainage Task Force, Annapolis, Maryland.

Belval, D. L. and L. A. Sprague. 1999. Monitoring nutrients in the major rivers draining to Chesapeake Bay. USGS Water-Resources Investigations Report 99-4238, Baltimore, Maryland.

Benitez, J. A. 2002. Historical land cover changes (1665–2000) and impact on N and P export from the Choptank watershed. Ph.D. Thesis, University of Maryland, College Park.

Benitez, J. A. and T. R. Fisher. 2004. Historical land cover conversion (1665–1850) in the Choptank watershed, eastern USA. *Ecosystems* 7: 219–232.

Benitez, J. A. and T. R. Fisher. In review. Land cover history (1665–2000), landscape patterns (1850–2000), and their effect on nutrient yields in the Choptank watershed, eastern USA. *Landscape Ecology*. au: update publication details if available.

Berndt, H. 1999. Effects of nutrients and turbidity from point and non-point source inputs on phytoplankton in the Choptank estuary. M.S. Thesis, University of Maryland, College Park.

Bernhardt, E. S., M. A. Palmer, J. D. Allan, G. Alexander, K. Barnas, S. Brooks, J. Carr, S. Clayton, C. Dahm, J. Follstad-Shah, D. Galat, S. Gloss, P. Goodwin, D. Hart, B. Hassett,, R. Jenkinson, S. Katz, G. M. Kondolf, P. S. Lake, R. Lave, J. L. Meyer, T. K. O'Donnell, L. Pagano, B. Powell, and E. Sudduth. 2005. Synthesizing U.S. river restoration efforts. *Science* 308: 636–637.

Cambell, J. E., D. B. Lobell, and C. B. Field. 2009. Greater transportation energy and GHG offsets from bio-electricity than ethanol. *Science* 324: 1055–1057.

Carlozo, N., G. Radcliffe, and T. R. Fisher. 2008. Trends in water quality in response to human populations and land use in the Delaware, Hudson, and Chesapeake Basins. Abstract, American Society of Limnology and Oceanography Conference, Orlando, Florida.

Clark, G. M., D. K. Mueller, and M. A. Mast. 2000. Nutrient concentrations and yields in undeveloped stream basins of the United States. *J. Am. Water Res. Assoc.* 36: 849–860.

Colt, J. 1984. Computation of dissolved gas concentrations in water as functions of temperature, salinity, and pressure. Am. Fish. Soc. Spec. Pub. 14, pp. 1–154.

Cooper, S. R. and G. S. Brush. 1993. A 2,500 year history of anoxia and eutrophication in Chesapeake Bay. *Estuaries* 16: 617–626.

Fisher, T. R., L. W. Harding Jr., D. W. Stanley, and L. G. Ward. 1988. Phytoplankton, nutrients, and turbidity in the Chesapeake, Delaware, and Hudson estuaries. *Estuar. Coastal Shelf Sci*. 27: 61–93.

Fisher, T. R., K.-Y. Lee, H. Berndt, J. A. Benitez, and M. M. Norton. 1998. Hydrology and chemistry of the Choptank River Basin in the Chesapeake Bay drainage. *Water Air Soil Pollut.* 105: 387–397.

Fisher, T. R., J. A. Benitez, K.-Y. Lee, and A. J. Sutton. 2006a. History of land cover change and biogeochemical impacts in the Choptank River Basin in the mid-Atlantic region of the US. *Int. J. Remote Sens.* 27: 3683–3703.

Fisher, T. R., J. D. Hagy III, W. R. Boynton, and M. R. Williams. 2006b. Cultural eutrophication in the Choptank and Patuxent Estuaries of Chesapeake Bay. *Limnol. Oceanogr.* 51: 435–447.

Fox, R. J., T. R. Fisher, T. M. Kana, and A. B. Gustafson. 2009. Concentration gradients of excess N_2 and N_2O in the vadose zone and groundwater of the mid-Atlantic coastal plain, U.S.A. Abstract, EGU, Vienna, Austria.

Glibert, P. M., D. J. Conley, T. R. Fisher, L. W. Harding, Jr., and T. C. Malone. 1995. Dynamics of the 1990 winter/spring bloom in Chesapeake Bay. *Mar. Ecol. Prog. Ser.* 122: 27–43.

Glibert, P. M., R. Magnien, M. W. Lomas, J. Alexander, C. Fan, E. Haramoto, M. Trice, and T. M. Kana. 2001. Harmful algal blooms in the Chesapeake and coastal bays of Maryland, USA: Comparisons of 1997, 1998, and 1999 events. *Estuaries* 24: 875–883.

Guillard, K. and K. L. Kopp. 2004. Nitrogen fertilizer form and associated nitrate leaching from cool-season lawn turf. *J. Environ. Qual.* 33: 1822–1827.

Hagy, J. D., W. R. Boynton, C. W. Keefe, and K. V. Wood. 2004. Hypoxia in Chesapeake Bay, 1950–2001: Long-term change in relation to nutrient loading and river flow. *Estuaries* 27: 634–658.

Hamilton, P. A., J. M. Denver, P. J. Phillips, and R. J. Shedlock. 1993. Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia: Effects of agricultural activities on, and distribution of, nitrate and other inorganic constituents in the surficial aquifer. US Geol. Surv., Open-File Rept. 93-40.

Harding, L. W., B. W. Meeson, and T. R. Fisher. 1986. Phytoplankton production in two east coast estuaries: Photosynthesis-light functions and patterns of carbon assimilation in Chesapeake and Delaware Bays. *Estuar. Coastal Shelf Sci*. 23: 773–806.

Harding, L. W., Jr. and E. S. Perry. 1997. Long-term increase of phytoplankton biomass in Chesapeake Bay. 1950–1994. *Mar. Ecol. Prog. Ser.* 157: 39–52.

Hively, W. D., C. J. Hapeman, L. L. McConnell, T. R. Fisher, C. P. Rice, G. W. McCarty, P. M. Downey, G. T. Nino de Gusman, K. Bialek, M. W. Lang, A. M. Sadeghi, D. R. Whitall, A. B. Gustafson, A. J. Sutton, K. A. Sefton, J. A. H. Fetcho. In review. Relating nutrient and herbicide fate with landscape features in 15 sub-basins of the Choptank River watershed: Implications for management. *Environ. Sci. Technol.* au: update Hively et al. if available

Jordan, T. E., D. L. Correll, and D. E. Weller. 1997. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. *J. Environ. Qual.* 26: 836–848.

Kana, T. M., C. Darkangelo, M. D. Hunt, J. B. Oldham, G. E. Bennett, and J. C. Cornwell. 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N_2, O_2, and Ar in environmental water samples. *Anal. Chem.* 66: 4166–4170.

Kana, T. M., M. B. Sullivan, J. C. Cornwell, and K. M. Groszkowski. 1998. Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. *Limnol. Oceanogr*. 43: 334–339.

Kana, T. M. and D. L. Weiss. 2002. Comment on "Comparison of isotope pairing and N2:Ar methods for measuring sediment denitrification" by B. D. Eyre, S. Rysgaard, T. Dalsgaard, and P. B. Christianson. *Estuaries* 25: 1077–1087.

Kemp, W. M., W. R. Boynton, J. E. Adolf, D. F. Boesch, W. C. Boicourt, G. Brush, J. C. Cornwell, T. R. Fisher, P. M. Glibert, J. D. Hagy, L. W. Harding, E. D. Houde, D. G. Kimmel, W. D. Miller, R. I. E. Newell, M. R. Roman, E. M. Smith, and J. C. Stevenson. 2005. Eutrophication of Chesapeake Bay: Historical trends and ecological interactions. *Mar. Ecol. Prog. Ser.* 303: 1–29.

Koroncai, R., L. Linker, J. Sweeney, and R. Batiuk. 2003. Setting and allocating the Chesapeake Bay Basin and sediment loads: The collaborative process, technical tools, and innovative approaches. US EPA Region III, Chesapeake Bay Program Office, Annapolis, Maryland.

Koskelo, A. I. 2008. Hydrologic and biogeochemical storm response in Choptank Basin headwaters. M.S. Thesis, University of Maryland, College Park.

au: update publication details if available. Koskelo, A. I., T. Jordan, and T. R. Fisher. In review. A new, precipitation-based method of base flow separation. *J. Hydrol.*

Lee, K.-Y., T. R. Fisher, and E. Rochelle-Newall. 2001. Modeling the hydrochemistry of the Choptank River basin using GWLF and Arc/Info: 2. Model Application. *Biogeochemistry* 56: 311–348.

Lowrance, R. L., S. Altier, J. D. Newbold, R. R. Schnabel, P. M. Groffman, J. M. Denver, D. L. Correll, J. W. Gilliam, J. L. Robinson, R. B. Brinsfield, K. W. Staver, W. Lucas, and A. H. Todd. 1997. Water quality functions of riparian forest buffer systems in Chesapeake Bay watersheds. *Environ. Manage.* 21: 687–712.

Marshall, H.G., T. Egerton, T. Stern, J. Hicks, and M. Kokocinski. 2004. Extended bloom concentrations of the toxic dinoflagellate *Dinophysis acuminata* in Virginia estuaries during late winter through early spring, 2002. Pp. 364–366, In: K. A. Steidinger, J. H. Landsberg, C. R. Tomas, and G. A. Vargo (eds.), *Harmful algae 2002*. Florida Fish & Wildlife Conservation Commission, Florida Institute of Oceanography, IOC of UNESCO, St. Petersburg, Florida.

McConnell, L. L. and G. W. McCarty. 2005. Annual report. CEAP Special Emphasis—Choptank River Watershed. 10/1/2004–9/31/2005, U.S. Department of Agriculture, ARS, Towson, Maryland.

Meade, R. H. 1968. Relations between suspended matter and salinity in estuaries of the Atlantic seaboard USA. *Internat. Assoc. Science Hydrol. General Assembly Bern* 4: 96–109.

Newell, R. I. E., T. R. Fisher, R. R. Holyoke, and J. C. Cornwell. 2004. Influence of eastern oysters on N and P regeneration in Chesapeake Bay, USA. In: R. Dame and S. Olenin (eds.), *The comparative roles of suspension feeders in ecosystems*. NATO Science Series: IV – Earth and Environmental Sciences. Dordrecht: Kluwer.

Norton, M. G. M. and T. R. Fisher. 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay. *Ecol. Eng.* 14: 337–362.

Officer, C. B., R. B. Biggs, J. L. Taft, L. E. Cronin, M. A. Tyler, and W. R. Boynton. 1984. Chesapeake Bay anoxia: Origin, development, and significance. *Science* 223: 22–27.

Primrose, N. L., J. L. Millard, P. E. McCoy, M. G. Sturm, S. E. Bowen, and R. J. Windschitl. 1997. German Branch Targeted Watershed Project: Report on 5 years of biotic and water quality monitoring 1990 through 1995. Chesapeake and Coastal Watershed Service, Watershed Restoration Division, Maryland Department of Natural Resources, Annapolis, Maryland.

Sellner, K. G. and S. Fonda-Umani. 1999. Dinoflagellate blooms and mucilage production. Pp. 173–206, In: T. C. Malone, A. Malej, L. W. Harding, Jr., N. Smodlaka, and R. E. Turner (eds.), *Ecosystems at the land-sea margin: Drainage basin to coastal sea*. Washington, D.C.: American Geophysical Union.

Staver, K. W. 2001a. *Increasing N retention in coastal plain agricultural watersheds*. Kirkkonummi, Finland: The Scientific World.

Staver, K. W. 2001b. The effect of agricultural best management practices on subsurface nitrogen transport in the German Branch watershed. Final Report, Maryland Department of Natural Resources, Project 14-198-34CZM025, Annopolis, Maryland.

Staver, K. W. and R. B. Brinsfield. 1998. Using cereal grain winter cover crops to reduce groundwater nitrate contamination in the mid-Atlantic coastal plain. *J. Soil Water Conserv.* 53: 230–240.

Staver, K. W., R. B. Brinsfield, and W. L. Magette. 1994. Tillage effects on phosphorus transport from Atlantic coastal plain watersheds. Pp. 215–222, In: P. Hill and S. Nelson (eds.), *Toward a sustainable coastal watershed: the Chesapeake experiment*. Proceedings of the 1994 Chesapeake Research Consortium Conference, Edgewater, Maryland.

Staver, L. W., K. W. Staver, and J. C. Stevenson. 1996. Nutrient inputs to the Choptank River Estuary: Implications for watershed management. *Estuaries* 19: 342–358.

au: update Stone et al. if details available.

Stone, J. P., T. R. Fisher, and R. Stone. In review. Water quality of non-tidal streams in Dorchester County, Maryland. *Water Air Soil. Pollut*.

Sutton, A. J. 2006. Evaluation of agricultural nutrient reductions in restored riparian buffers. Ph.D. Thesis, University of Maryland, College Park.

Sutton, A. J., T. R. Fisher, and A. B. Gustafson. 2009a. Historical changes in water quality at German Branch in the Choptank River Basin. *Water Air Soil Pollut*. 199: 353–369.

Sutton, A. J., T. R. Fisher, and A. B. Gustafson. 2009b. Effects of restored stream buffers (CREP) on water quality in non-tidal streams in the Choptank River Basin. *Water Air Soil Pollut*. DOI 10.1007/s11270-009-0152-3.

Tango, P., W. Butler, R. Lacouture, D. Goshorn, R. Magnien, B. Michael, S. Hall, K. Brohawn, R. Wittman, and W. Beatty. 2002. An unprecedented bloom of *Dinophysis acuminate* in Chesapeake Bay. Pp. 358–360, In: K. A. Steidinger, J. H. Landsberg, C. R. Tomas, and G. A. Vargo (eds.), *Harmful algae 2002*. Florida Fish & Wildlife Conservation Commission, Florida Institute of Oceanography, IOC UNESCO, St. Petersburg, Florida.

Tilman, D., J. Hill, and C. Lehman. 2006. Carbon-negative biofuels from low-input high diversity grassland biomass. *Science* 314: 1598–1600.

Tilman, D., R. Socolow, J. A. Foley, J. Hill, E. Larson. L. Lynd, S. Pacala, J. Reilly. T. Searchinger, C. Somerville, and R. Williams. 2009. Beneficial biofuels: The food, energy, and environment trilemma. *Science* 325: 270–271.

Traband, J. J. 2003. Removal of wastewater nitrogen and phosphorus by an oligohaline marsh. MS Thesis, University of Maryland.

U.S. Environmental Protection Agency. 2000. Information supporting the development of state and tribal nutrient criteria for rivers and streams in nutrient ecoregion XIV. EPA 822-B-00-022. Washington, D.C.: US EPA.

U.S. Environmental Protection Agency. 2007. Ambient water quality criteria for dissolved oxygen, water clarity and chlorophyll *a* for the Chesapeake Bay and its tidal tributaries—Chlorophyll *a* Addendum. October 2007. EPA 903-R-07-005. Region III Chesapeake Bay Program Office, Annapolis, MD.

Valderrama, J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Mar. Chem*. 10: 109–122.

Vitousek, P. M., R. Naylor, T. Crews, M. B. David, L. E. Drinkwater, E. Holland, P. J. Johnes, J. Katzenberger, L. A. Martinelli, P. A. Matson, G. Nziguheba, D. Ojima, C. A. Palm, G. P. Robertson, P. A. Sanchez, A. R. Townsend, and F. S. Zhang. 2009. Nutrient imbalances in agricultural development. *Science* 324: 1519–1520.

Wazniak, C. E., M. R. Hall, C. Cain, D. Wilson, R. Jesien, J. Thomas, T. Carruthers, and W. C. Dennison. 2004. State of the Maryland Coastal Bays Report, Annapolis, Maryland.

Williams, M. R., T. R. Fisher, K. N. Eshleman, W. C. Boynton, W. M. Kemp, C. F. Cerco, S.-C. Kim, R. R. Hood, D. A. Fiscus, and G. Radcliffe. 2006. An integrated modeling system for management of the Patuxent River Estuary and Basin, Maryland, USA. *Int. J. Remote Sens.* 27: 3705–3726.

Winter, T. C. 1983. The interaction of lakes with variably saturated porous media. *Water Res. Res.* 19: 1203–1218.

Wrage, N., G. L. Velthof, M. L. Beusichem, and O. Oenema. 2001. Role of nitrified denitrification in the production of nitrous oxide. *Soil. Biol. Biochem*. 33: 1723–1732.