

Quantifying Groundwater's Role in Delaying Improvements to Chesapeake Bay Water Quality

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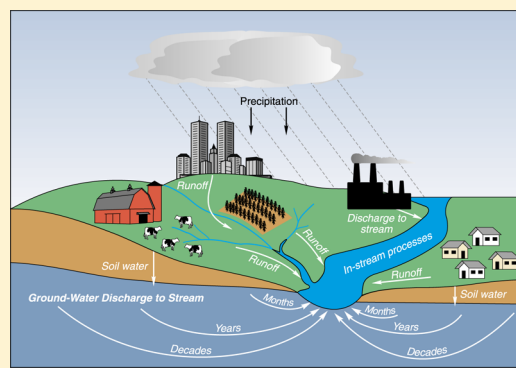
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S Supporting Information

ABSTRACT: A study has been undertaken to determine the time required for the effects of nitrogen-reducing best management practices (BMPs) implemented at the land surface to reach the Chesapeake Bay via groundwater transport to streams. To accomplish this, a nitrogen mass-balance regression (NMBR) model was developed and applied to seven watersheds on the Delmarva Peninsula. The model included the distribution of groundwater return times obtained from a regional groundwater-flow (GWF) model, the history of nitrogen application at the land surface over the last century, and parameters that account for denitrification. The model was (1) able to reproduce nitrate concentrations in streams and wells over time, including a recent decline in the rate at which concentrations have been increasing, and (2) used to forecast future nitrogen delivery from the Delmarva Peninsula to the Bay given different scenarios of nitrogen load reduction to the water table. The relatively deep porous aquifers of the Delmarva yield longer groundwater return times than those reported earlier for western parts of the Bay watershed. Accordingly, several decades will be required to see the full effects of current and future BMPs. The magnitude of this time lag is critical information for Chesapeake Bay watershed managers and stakeholders.



INTRODUCTION

Nitrate is one of the most widespread contaminants in streams and shallow aquifers in the United States,^{1–3} with fertilizer applied in agriculture being one of the dominant sources of nitrogen. The Chesapeake Bay watershed contains a number of streams and rivers with elevated levels of nitrate that feed into and adversely affect the water quality of the Bay.^{4,5} Much of the nitrate in the streams and rivers is derived from groundwater that discharges as base flow,^{4,6} as many areas, especially those with agriculture, have elevated levels of nitrate in shallow groundwater.⁷ The U.S. Environmental Protection Agency (USEPA) has been working with the local states to reduce loading of nitrogen to the Bay by developing a watershed model⁸ to help quantify the distribution of nitrogen sources within the watershed and forecast future water quality conditions in the Bay. The USEPA Chesapeake Bay Partnership (CBP) watershed model also accounts for actions taken by local stakeholders to help reduce nitrate runoff, usually in the form of implementing best management practices (BMPs) such as planting winter cover crops^{9,10} or establishing forest buffer zones adjacent to streams.^{11,12}

The USEPA-CBP model is predominantly a surface water model with a groundwater storage component to simulate transient flow conditions, but the nutrient components of the

model do not account for the lag time of nitrate passing through the groundwater system. In terms of water-quality management, the lag time is the time between implementing improved pollution-management practices on the ground and seeing the improved water quality in the stream. This lag time between implementation and result is a great concern for water quality managers and regulators¹³ because society usually desires a relatively quick return on our investments, and may begin to doubt the effectiveness of the actions if beneficial results are delayed too long. Groundwater return times (the time required for recharge at the water table to return to a stream through groundwater) within most areas of the Chesapeake Bay watershed have been documented to range typically from years to decades.^{14,15} In particular, long-term tritium records from the Susquehanna and Potomac Rivers have revealed that approximately half of the water discharging is greater than one-year old, with the mean age of the older fraction for the two rivers being ten and twenty years, respectively.¹⁶ Given that the distribution of the age of groundwater

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that discharges as base flow usually follows a logarithmic pattern with a long tail of old ages,^{17,18} the effect from fertilizer application or fertilizer reduction at the land surface in many areas can be expected to take decades to reach its full extent in terms of flux to the stream.¹⁹ Because fertilizer application in the Chesapeake Bay watershed rose dramatically during the 1960s and 1970s,^{14,15} many local watersheds are not yet at a steady-state condition with respect to nitrate. Groundwater return times need to be accounted for if trends in nitrate concentrations in many of the streams in the Bay watershed are to be adequately explained. In addition, if forecasts of future stream loads to the Bay and assessments of the long-term effectiveness of BMPs are to be reliable in a temporal context, groundwater return times need to be included in the accounting.

The objective of this study was to create a model which could forecast future nitrogen loadings to the Bay by including the effects of groundwater return times. A nitrogen mass-balance regression (NMBR) model was developed to simulate nitrate concentrations that could be matched against those observed in wells and streams in several watersheds across the Delmarva Peninsula (Figure 1). The Delmarva was chosen because of its proximity to the Bay, its high nitrogen yields,^{20,21} the availability of a well-calibrated groundwater-flow (GWF) model,²² and its thick, porous surficial aquifer that represents the setting of the Coastal Plain Province, which in turn represents a substantial source of the overall nitrogen entering the Bay.²¹ In order to forecast future nitrate delivery to the Bay from the peninsula, the NMBR model had to incorporate the history of fertilizer use and the distribution of groundwater return times to streams within the peninsula. The groundwater return times were obtained from a recently developed GWF model of the shallow aquifer system of the Delmarva Peninsula.²² In addition to the fertilizer-use (both inorganic and manure) history and groundwater return times, the NMBR model includes denitrification parameters and an improvement factor for uptake efficiencies that represented any improvements in nutrient management practices over time. The NMBR model was used to forecast future nitrogen loading to the Bay given different future load-reduction scenarios at the land-surface.

MATERIALS AND METHODS

Groundwater-Flow (GWF) Model. The GWF model is a three-dimensional, steady-state flow model of the shallow aquifer system of the Delmarva Peninsula, constructed using the United States Geological Survey (USGS) code MODFLOW.²³ Details of the model grid construction were documented in an earlier report.²² The key components in the determination of groundwater return times are the recharge rate, the depth of the flow system, and the porosity.²⁴ The depth of the shallow flow system in the GWF model was incorporated using a digital geologic framework, which established the location and depths of the southeasterly dipping coastal plain formations that typically alternate between sand-rich aquifers and clay-rich aquitards. Quaternary-age permeable sands overly these formations across most of the peninsula. The porosity value for the model was adjusted to fit the value of groundwater ages measured using chlorofluorocarbon concentrations (CFCs) and tritium-helium ratios at 24 wells located across the peninsula.²⁵ A value of porosity of 0.35 was calibrated to be the best fit for all of the formations, and was consistent with values measured on samples of the unconsolidated sediments in these surficial formations.²⁶ Other parameters in

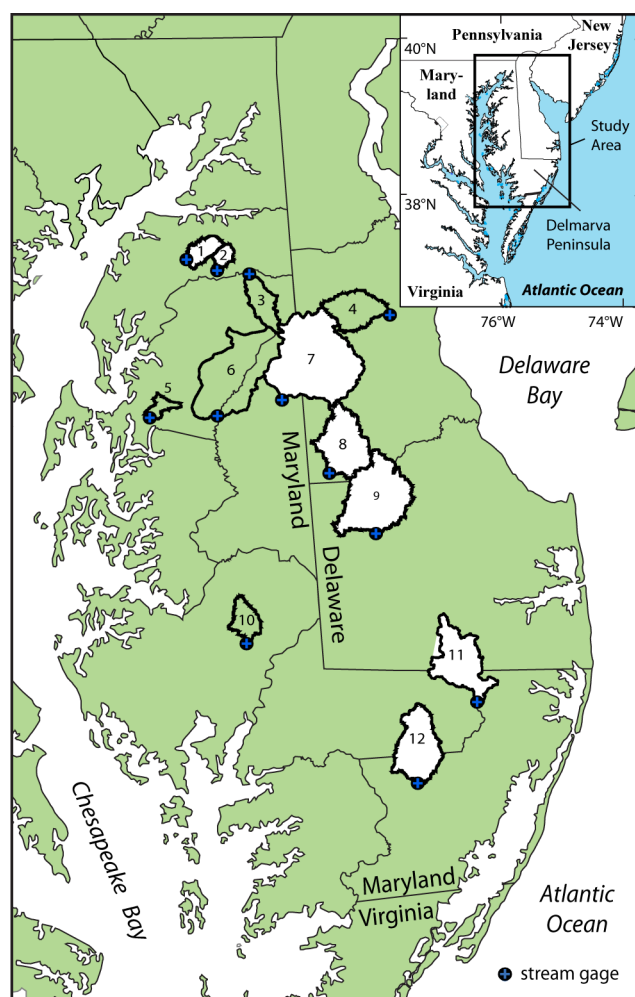


Figure 1. Locations of USGS stream gages and watersheds on the Delmarva Peninsula with real-time flow and water quality data used in this study. Watersheds in white have historical stream-nitrate concentration data that were used to calibrate the nitrogen mass-balance regression (NMBR) model. See Table 1 for details associated with numbered watersheds.

the model, such as hydraulic conductivity values of aquifers and confining units, were calibrated against numerous water levels in wells.²²

Although recharge rates can be estimated using a variety of techniques,²⁷ the rate across the peninsula was determined by using a water-balance regression (WBR) model²⁸ developed for Virginia that included the Delmarva Peninsula.²⁹ Long-term recharge is calculated in the WBR model based on the assumption that recharge is equal to the precipitation minus the surface runoff minus evapotranspiration. The precipitation and ET were obtained and calculated from climate data.³⁰ The surface runoff was estimated from chemical hydrograph separations^{31,32} on a number of streams in the coastal plain,²⁹ and determined by regression to be a strong function of the sediment size of the surficial formation. In the WBR model the surface runoff fraction of total runoff averaged about 0.15 (Table 1), and was varied as a function of the clay content of the soil. This fraction underscores the dominance of groundwater in delivering nitrogen to streams on the Delmarva Peninsula.¹⁵ In the GWF model the recharge rates from the WBR model along with “drain” boundary conditions were assigned everywhere at the land surface—a method that allows

Table 1. Age Composition of Streamflow and Base Flow in Streams at Real-Time USGS Gages on the Delmarva Peninsula Based on Groundwater-Flow (GWF) Model Results^{22 a}

USGS real-time gage number	stream name	surface runoff	groundwater discharge					
		high flow ^c		base flow age ^d				
		hours to days old	>days and <1 year old ^b	1 to <7 years old	7 to <13 years old	13 to <50 years old	≥ 50 years old	median base-flow age (years)
01493500	Morgan Creek	16.4	10.1	10.5	7.7	20.6	34.7	40
01493112	Chesterville Branch	15.5	3.8	8.4	9.2	30.2	32.8	28
01491000	Choptank River	15.0	18.1	10.1	8.8	23.8	24.2	27
01488500	Marshyhope Creek	15.6	17.2	10.4	8.6	29.4	18.8	25
01487000	Nanticoke River	14.0	12.3	13.0	11.2	34.5	15.0	20
01485000	Pocomoke River	14.8	14.0	4.9	4.8	32.5	29.0	34
01485500	Nassawango Creek	15.6	9.2	6.2	8.1	30.2	30.8	32
average of seven watersheds		15.3	12.1	9.1	8.3	28.7	26.5	29.4
composite values		hours to <1 year old		1 to <7	7 to <13	≥13 years old		same
average of seven watersheds		27.4		9.1	8.3	55.2		29.4
earlier USGS estimate for Chesapeake Bay Watershed ¹⁴		50.0		12.5	25	12.5		10

^aA comparison is made to an earlier estimate¹⁴ of base-flow ages for the Chesapeake Bay watershed. All values are percent of total streamflow unless otherwise indicated. ^bBased on the amount of simulated rejected recharge in the groundwater flow model. In this study rejected recharge at each cell is defined as the minimum value of either the water-balance regression (WBR) recharge applied at the cell, or the drain-discharge flux at the cell. ^cDefined as the flow rate above which nitrate concentrations decrease with increasing flow. ^dBased on the groundwater return times simulated in the groundwater flow model.

the model to naturally determine the groundwater discharge locations and rates in the stream networks.³³

The GWF model was used to determine the distribution of base-flow ages to the streams by using the USGS model MODPATH,³⁴ which allows the calculation of a groundwater travel time along any given flow pathline within a MODFLOW model. A groundwater pathline was traced (and travel time calculated) from every recharge cell in the GWF model on the peninsula to its discharge location either at a stream or coastal cell. These groundwater return times (base-flow ages) calculated using MODPATH with the GWF model were compiled and used in the NMBR model. An earlier local cross-sectional model³⁵ was used in this way to estimate groundwater ages in the shallow Delmarva aquifer, and yielded ages similar in range to those of the GWF model.²²

Nitrogen Mass-Balance Regression (NMBR) Model. In order to explain both the spatial and temporal trends in stream and groundwater nitrogen concentrations, a NMBR model was created that began with (1) the loading of nitrogen across the land surface over time, (2) dissolving that nitrogen in the recharge and tracking and timing its path through the aquifer to the seven streams, and (3) allowing for nitrogen loss along the way by plant uptake and denitrification in order to (4) calculate the final concentrations of nitrate in the streams at the measurement sites. Calculations were made for step (1) using the fertilizer and manure input histories, step (2) using the GWF model, and by combining these with steps (3) and (4) using the following equations to calculate a mean base-flow concentration in a stream for the year it was sampled:

$$C_s = (1 - D_s)(1 - D_r) \sum_{i=1}^{Nyr} \left(\left(\frac{Q_{iag}}{Q_t} \right) C_{iag} + \left(\frac{Q_{ina}}{Q_t} \right) C_{na} - D_g t_i \right) \quad (1)$$

$$\text{and } C_{iag} = (L_{if}(1 - E_f) + L_{im}(1 - E_m)) / (R_w A_w) \quad (2)$$

where C_s is the mean nitrate concentration for a stream for a given year, $[ML^{-3}]$, D_s and D_r are soil and riparian denitrification factors (dimensionless), Nyr is the number of yearly base-flow-age bins ($=200$), (Q_i/Q_t) is the fraction of base flow of that age within the stream's total base-flow (dimensionless), C_{iag} and C_{na} are concentrations of nitrate in recharge $[ML^{-3}]$, D_g is a groundwater denitrification factor $[ML^{-3}t^{-1}]$, t_i is the base-flow age (t), L_i is an annual nitrogen application (load) at the land surface (M), E is an uptake efficiency (dimensionless), R_w is the mean annual recharge for a watershed (Lt^{-1}), A_w is the area of a watershed (L^2), and the subscripts r , ag , na , f , and m correspond to recharge, agricultural, nonagricultural, inorganic fertilizer, and poultry manure, respectively. Groundwater denitrification could have been represented as either a zero or first order loss term, depending on whether the loss rate is constant in time or a function of concentration. D_g in eq 1 is listed as a zero-order loss term, and the parameter estimation revealed that the available data were not sufficient to constrain a parameter for either a zero- or first-order term independently from the other denitrification terms using this approach. As the nitrate data are scattered among various watersheds at various times and not along a single or a few well-defined flow paths, they do not lend themselves to determining the physical process by which soil and riparian denitrification are occurring, and thus the two terms are simple multipliers to estimate the fraction of nitrate that is lost to each process by their correlation with soil-drainage character and stream length. Equations 1 and 2 were applied to each of the seven watersheds at each of the years for which nitrate concentrations were observed and simulated over time (Table 1, Figure 1). More details of the implementation of eqs 1 and 2 are in provided in the Supporting Information (SI).

Fertilizer application data was taken from inorganic fertilizer sale data compiled by the USGS.^{36,37} Poultry manure application estimates were obtained from past agricultural census data of poultry.^{37,38} Both of these data sets were available only at the county levels.³⁹ Soybeans also contribute substantial nitrogen to the subsurface by nitrogen fixation, but the net addition to the subsurface is relatively small compared to fertilizer and manure inputs,⁴⁰ and thus nitrogen fixation and removal by soybeans were not included in the NMBR model. Atmospheric deposition contributes substantial nitrogen to the Chesapeake Bay as a whole,²¹ but it is a small fraction (4%) of the total load in its agricultural watersheds.²⁰ For this reason, and because there were no available data for how atmospheric loadings have increased during the 20th century, the atmospheric deposition load was assumed to be negligible in C_{ag} in eq 1, but was considered to be the main contributor of nitrate that accounts for C_{na} . C_{na} was given the value of 0.15 mg/L, a typical value from wells located in the study area in either forests or wetlands (see SI, Figure S-2). Watersheds that covered multiple counties were weighted by the fraction of the watershed occurring in each county. The use of inorganic fertilizer and poultry manure has increased several fold since World War II, but the quantity applied on the peninsula has stabilized in the last few decades.^{36,37} This increase in fertilizer use has been linked to the increases in nitrates seen in the stream concentrations on the peninsula.^{41,42} Details of the fertilizer data are provided in the SI.

The simulated nitrate concentrations for the streams and wells were compared with observed concentrations between the years 1961 and 2012 that were combined into multiyear average values for the purpose of the parameter optimization. In order to attempt to account for improvements in fertilizer management practices that have been occurring over the last few decades, and to see whether or not such improvements were detectable in the data, one additional parameter, E_{time} (t^{-1}), was included, wherein both uptake efficiencies, E_f and E_m , were multiplied by a value that increased linearly from zero to E_{time} between the year 1970 and 2000. These three fertilizer uptake parameters and three denitrification parameters (D_s , D_r , and D_g) were adjusted until a best fit was obtained between the simulated and observed concentrations. The best fit parameters were used along with eqs 1 and 2 to all of the watersheds draining the Delmarva Peninsula to the Bay to calculate of the total annual load of nitrate in base flow. The total dissolved nitrogen (TDN) loading to the Bay over time was then estimated by adding observed dissolved organic nitrogen (DON) values to the base-flow and high-flow concentrations, which were then multiplied by their corresponding flow rates (see below).

RESULTS

Base-Flow Age Distribution. The groundwater discharging to the streams in the seven watersheds used for nitrate calibration in this study (Figure 1) had simulated ages that ranged from <1 year to centuries, with median ages ranging from 20 to 40 years (Table 1). The cutoff between base flow and high flow in Table 1 was defined as the streamflow rate at which the nitrate concentration in the stream began to decrease with increasing flow rate (see SI, Figures S-10, S-11). The groundwater age distributions are markedly older than previously estimated for the more western regions of the Chesapeake Bay Watershed (Table 1, Figure 2), which have terrains dominated by fractured-rock with relatively thin overburdens and lower

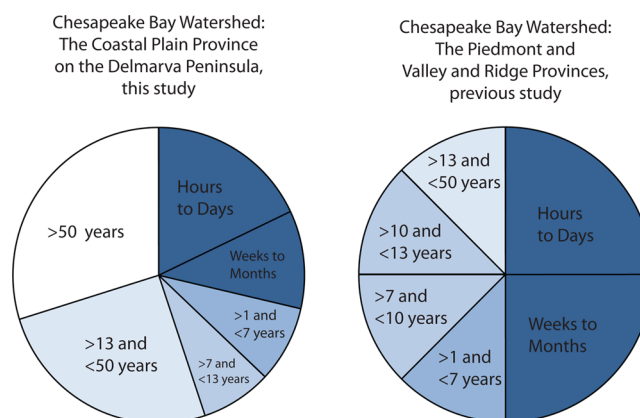


Figure 2. Estimated distribution of base-flow age for the Chesapeake Bay watershed on the Maryland and Delaware sections of the Delmarva Peninsula based on a groundwater-flow (GWF) model of the region,²² compared to earlier estimates for the Chesapeake Bay watershed¹⁴ that were from data in the Piedmont and Valley and Ridge Provinces west and north of the Bay.

bedrock porosities. The earlier age distribution estimate was made from a study⁴³ that only sampled CFCs in springs, less than 5% of which were from the Coastal Plain Province, and none of which were east of the Bay. Concentrations of CFCs in springs are particularly difficult to interpret⁴⁴ because they represent a nonlinear mixture of ages and can contain CFCs from small point contaminations that are undetectable yet can bias the interpreted age to appear too young. Greater than 50% of the groundwater discharging to streams is older than 13 years in the current study, compared to less than 15% being older than 13 years in the earlier study.^{6,43} The GWF model results indicated that the spatial distribution of groundwater return times across the Peninsula is highly correlated to the stream network,²² as recharge close to the streams has a relatively quick return time compared to recharge closer to the watershed divides.

NMBR Model Calibration. At the start of the NMBR equation calibration only two parameters were estimated, and then additional parameters were added⁴⁵ until finally six were estimated (Table 2). The sum of squared weighted residuals for each regression continued to decline as each additional parameter was added. The standard error of regression also declined, indicating that the additional parameter contributed significantly to the fitting process.⁴⁶ The initial regression included only the fertilizer and manure uptake efficiencies with no denitrification. For this case the optimal values for the fertilizer and manure uptake efficiencies were calculated to be 86 and 75%, respectively. The soil-zone and riparian denitrification terms were added individually and then together, with the combined optimal exponents being 0.554 and −0.14, respectively. The soil-zone term calibration was based on a soil-drainage classification rank between 1 and 6, where a value of 1 (a very poorly drained soil) resulted in about 45% denitrification and a value of 6 (a very well drained soil) in 0% denitrification. The riparian denitrification term was a function of the area of the watershed where an equivalent distance of travel along a stream resulted in about 10% denitrification in the first 3 km, and about 50% denitrification after 30 km. The parameter for groundwater denitrification, D_g , was estimated to be close to zero, but in situ is likely to have a small finite value. The near-zero value is consistent with the well-oxygenated waters

Table 2. Best-Fit Values of Parameters and Their Sensitivities for the Nitrogen Mass-Balance Regression (NMBR) Equation^a

regression number	fertilizer uptake efficiency pre-1970, E_f	manure uptake efficiency pre-1970, E_m	percent increase in uptake efficiencies 1970–2000, E_{time}	fertilizer uptake efficiency post-2000, E_f	manure uptake efficiency post-2000, E_m	riparian and Stream loss exponent for riparian denitrification, D_r	unsaturated zone (soil) loss exponent for soil denitrification, D_s	rate of loss in the saturated zone, in mg per liter per year, D_g	number of parameters estimated	sum of squared weighted residuals	standard error of regression	R-squared value for observed versus simulated temporal stream data ^b	slope of best fit line for observed temporal stream data ^c
1	86%	75%	0	86%	75%	0	0	0	2	8987	130	0.774	0.672
2	81%	61%	0	81%	61%	0	1.17	0	3	6074	88	0.920	0.886
3	77%	54%	0	77%	54%	−0.129	0	0	3	3926	57	0.877	0.751
4	74%	36%	0	74%	36%	−0.14	0.554	0	4	2529	37	0.929	0.906
5	66%	40%	23%	81%	49%	−0.117	0.572	0.00	5	2173	32	0.959	0.894
10% upper parameter value limit [§]	73%	48%	42%	NA	NA	−0.103	0.86	0.19	5	2390	40	NA	NA
10% lower parameter value limit [§]	62%	27%	5%	NA	NA	−0.143	0.35	0.00	5	2390	40	NA	NA
10% limits as percent of value	8%	26%	80%	NA	NA	17%	45%	NA	5	2390	40	NA	NA

^aSee SI for definition of the nitrate-loss parameters in the NMBR equation. NA = not applicable. ^bMorgan Creek, Nanticoke River, and Choptank River data. ^cIndicates the highest or lowest value of the parameter that will not cause the sum of squared weighted residual to exceed 10% of the minimum value when the other parameters are allowed to vary.

present in most of the shallow Delmarva, and in situ denitrification of this type is known to be occurring in other localities in the Mid-Atlantic Coastal Plain.⁴⁷

Three watersheds in particular: Morgan Creek, Choptank River, and Nanticoke River have base-flow nitrate observations that cover several decades (Figure 3). Fourteen of the 25 total observations used in the parameter estimation were multiyear average concentrations from these three watersheds. The NMBR eqs 1 and 2 were used to estimate the nitrate concentrations in these rivers over time using the four optimized parameter values E_f , E_m , D_s , and D_r (D_g set to zero). The differences between the simulated and observed multiyear concentrations averaged 5, 8, and 12% for Morgan Creek, Choptank River, and Nanticoke River, respectively (Figure 3). Given denitrification and uptake efficiencies vary spatially, exact matches between simulated and observed values for all three watersheds with a single set of parameters were not expected. The objective of this study, however, was to quantify the total nitrogen loading to the Bay and its transient response to changes in nitrogen loading to the water table, and thus only one set of best-fit parameters was estimated and used in the final load calculation.

The last parameter, E_{time} , was estimated to account for the potential effects of previously implemented nutrient management practices that might be reducing the amount of nitrate reaching the water table. The result of including E_{time} was that a new better fit was obtained by allowing the uptake efficiencies to improve by 23% (Table 2). The final model had uptake efficiencies, E_f and E_m , of 66 and 40% before 1970 and 81 and 49% after 2000, with a linear increase applied in between. These estimated uptake percentages are in general agreement with nitrogen budgets for agricultural regions.⁴⁰ The resulting effect on the simulation was that the nitrate concentrations in the streams began to plateau in the 1990s and 2000s to a greater extent than they would without this improvement (Figure 3). An uncertainty analysis (Table 2) indicates the estimated value of E_{time} was substantially less certain than the estimates of E_f and E_m .

Chesapeake Bay TDN Load Estimate for 2009. In order to estimate the TDN load to the Bay (and compare with current USEPA estimated and target loadings), the calibrated NMBR equations were applied to the 41 HUC-11 watersheds that comprise the section of the Peninsula that drains into the Chesapeake Bay. The mean high flow rate was estimated in each HUC-11 watershed by using the linear relationship that was observed in the MODFLOW simulations between the percent of streamflow that is rejected recharge and the observed percent of streamflow in the streams that exceeded the nitrate base-flow cutoff value (SI, Figure S-11). The mean high-flow nitrate concentration was estimated to be 65% of the base-flow concentration, a value consistently observed in the streams (SI). Total dissolved organic nitrogen (TDON) loads were added to the base-flow and high-flow nitrate loads to obtain estimated TDN loads for the HUC-11 watersheds. DON values of 0.37 and 0.63 mg N per liter were used, which were the observed means of several streams on the peninsula in manure poor and rich regions, respectively. Dissolved ammonia values were not included as they represent at most only a few percent TDN concentrations (SI, Figure S-3). The fraction of the total groundwater discharge that is occurring directly to the Bay along the shoreline or tidal estuaries has been shown to quite small (<0.05),⁴⁸ and thus this study includes only groundwater discharge to nontidal streams in the total load calculations.

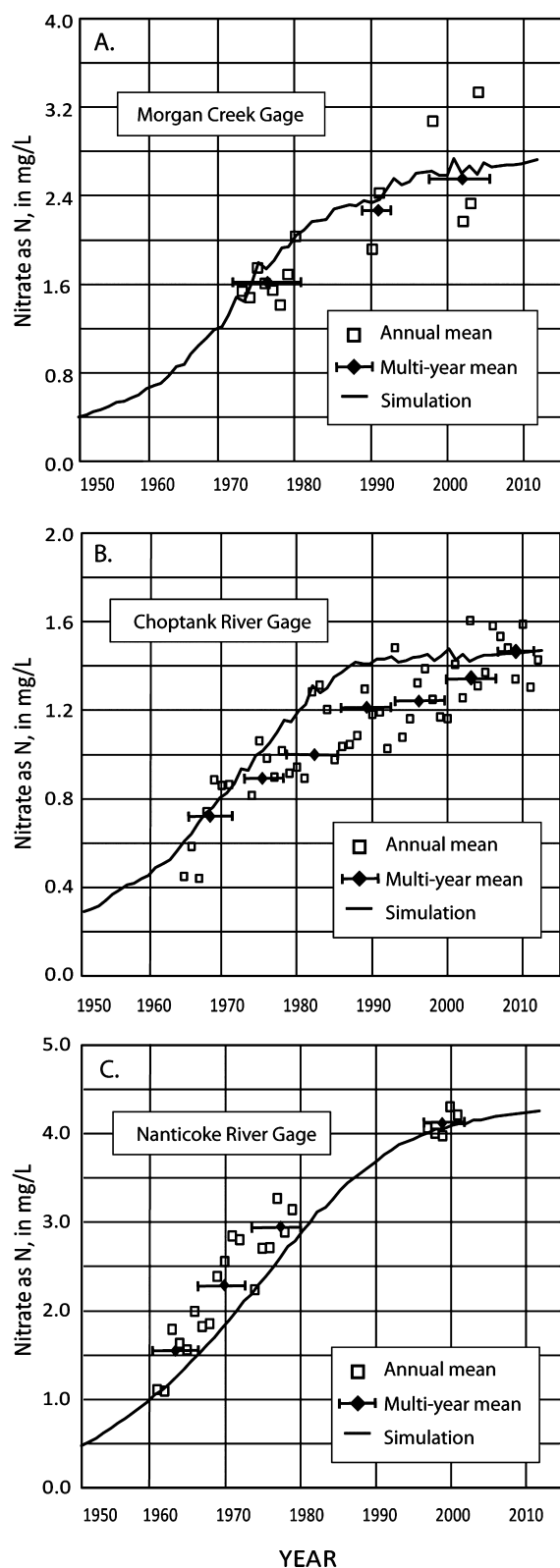


Figure 3. Observed nitrate concentrations in base flow at (A) Morgan Creek near Kennedyville, MD, (B) Choptank River near Greensboro, MD, and (C) Nanticoke River near Bridgeville, DE, and simulated values using the calibrated parameters of the nitrogen mass-balance regression (NMBR) model.

The final estimated TDN load to the Chesapeake Bay from the Delmarva Peninsula study area was 6400 t for 2009 (Figure 4). USEPA reported an estimated total stream TN load for this

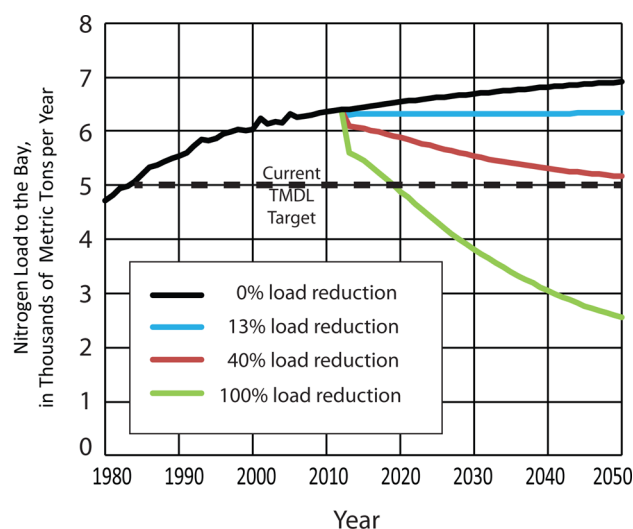


Figure 4. Forecast of total dissolved nitrogen (TDN) loading to the Chesapeake Bay from total streamflow from the Delmarva Peninsula study area based on the nitrogen mass-balance regression (NMBR) model that incorporated the simulated distribution of groundwater return times from the groundwater-flow (GWF) model. The dashed horizontal line represents the approximate 25% reduction TMDL target for this region proposed by the U. S. Environmental Agency in conjunction with the local states.⁴⁹

study region in 2009 of 17 million pounds (7700 t).⁴⁹ The USEPA estimate may be slightly higher than the NMBR model estimate for a few reasons, most likely because the NMBR watersheds had no point sources of nitrogen, such as urban or wastewater-treatment plant sources, and did not account for suspended particulate nitrogen (TN versus TDN). TN data were not available in sufficient quantity on the Delmarva to include in the NMBR model, and those that do exist are very close to TDN values. The magnitude of the difference between the EPA and NMBR 2009 load estimate is consistent with these differences in sources and the measured nitrogen data used.

Chesapeake Bay TDN Load Future Forecast. The future TDN total streamflow load forecast to the Chesapeake Bay from the study area using the NMBR model included all six calibrated parameters and a constant future application rate of fertilizer and poultry manure equal to the average rate for 2008–2012. Given this scenario, this TDN load is predicted to continue to rise to almost 7000 t by the year 2050 (Figure 4). This future rise is caused by the lag in the groundwater response time—low-nitrate old groundwater currently discharging into the streams will no longer be low in nitrate as time progresses. Thus, if there is a zero percent load reduction of nitrogen to the water table, the nitrogen load to the Bay is forecast to continue to rise by 13% by 2050 relative to the 2012 load. The NMBR model was also used to forecast future TDN loads to the Bay if nitrogen reductions to the water table are made after 2012. Conversely, a load reduction of 13% to the water table is required to cause the TDN load to the Bay to remain constant into the future at the 2012 level. A load reduction at the water table of 40% would cause the TDN load to the Bay to decrease down to about 5000 t by the year 2050. Similarly a complete removal of nitrogen entering the water Table (100% load reduction) would cause the TDN load to decrease down to about 5000 and 2500 t by the years 2020 and 2050, respectively. A sensitivity analysis on how the estimated parameters affect the model forecasts was performed and the results are

described in the SI (Figure SI-17). Nearly all of the parameters affect only the total load to the Bay being estimated, and not the response time of the system. In addition, uncertainty in input data such as fertilizer loading would affect only the parameters (such as the uptake efficiencies) that control the magnitude of the estimated load and not the temporal effect of the groundwater lag times.

DISCUSSION

The USEPA, together with the states, have made target TMDL goals and reduction goals for the Bay. These goals may be adjusted in the future, but currently the reduction goal for the Maryland and Delaware portions of the Delmarva Peninsula is approximately 25% of the 2009 load, which would correspond to about 5000 t TDN per year by 2020.⁴⁹ This value is not the load the Bay would be receiving in 2020, but only what would ultimately lead to a load of 5000 t TDN by having a certain amount of BMPs implemented by 2020. The current Chesapeake Bay HSPF model,⁸ which is being used by the USEPA to calculate these load reduction targets, or total maximum daily load (TMDL) requirements, bases its calculations of stream loadings from the spatial regression model SPARROW.^{20,21} It does not consider any groundwater lag times or other transient loading effects. It only predicts what the final reduction in load to the Bay would be given the implementation of BMPs and their corresponding anticipated effects. The forecasts in this study show reduced nitrogen loading to the water table takes decades to be fully observed in streams. Given that a 13% reduction in load to the water table is required to maintain the current load to the Bay, a 25% load reduction to the water table would ultimately only lead to a 12% load reduction to the Bay. Although the USEPA is aware of the potential effects of groundwater lag times, the magnitude of these effects have not yet been quantified or accounted for. The forecasts in this study, based on the best estimates of the groundwater conditions on the peninsula, indicate several decades will be required to flush out the groundwater reservoir to the extent that the targeted reductions could be realized.

Other aspects of the results of this study suggest that nutrient management practices, implemented over the past decade especially, have begun to work and, thus, could continue to work in the future as they are expanded. If the parameter E_{time} is set to zero (no effect from nutrient management so far), the model predicts the current load to the Bay would be 8200 rather than 6400 t. So although the TDN loads are still currently rising, this study suggests they are not at the level they could have been if uptake efficiencies had not been improving. Also, some of the most effective practices, such as the use of cover crops, have been implemented mostly within the last several years.⁵⁰ This more recent effect may not be fully observed yet in the data, and thus does not yet appear in the NMBR model forecast. The most likely variable that might cause the NMBR forecast to deviate substantially (especially at more local scales) is the uncertainty in the base-flow age distributions.¹⁷ The GWF model is regional in nature and could not take into effect local aquifer heterogeneities that can affect base-flow age distributions. However, the NMBR model is designed to highlight the magnitude of the overall regional system response time, rather than to accurately predict details of future fluxes. For load reduction to the Bay, nitrogen load has only to be reduced at the water table, not the application rate to the land surface, so reductions to the Bay could be realized by improved and additional BMPs, not necessarily by

reductions in fertilizer or manure application rates. The results of this study highlight the large difference in times between USEPA's target of several years for BMPs to be in place and the many decades before these practices would lead to the desired reductions in nitrogen loading to the Bay. There are many stakeholders invested in restoring the health of Chesapeake Bay, and the delay that groundwater will cause in improvements to its water quality must be a well understood factor in its undertaking.

ASSOCIATED CONTENT

Supporting Information

Additional Supporting Information is available in the form of text, tables, and figures, describing in more detail the calculation methods and inputs into the GWF and NMBR models and results, including a sensitivity analysis of the nitrogen forecast to the Bay to the NMBR parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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