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Quantifying the Response of Nitrogen Speciation to Hydrology in the Chesapeake Bay Watershed Using a Multilevel Modeling Approach

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Research Impact Statement: Increased riverine nitrogen due to increased anthropogenic inputs may enrich the inorganic fraction while increased riverine nitrogen due to hydrologic factors may deplete the inorganic fraction.

ABSTRACT: Excessive nitrogen (N) inputs to coastal waters can lead to severe eutrophication and different chemical forms of N exhibit varying levels of effectiveness in fueling primary production. Efforts to mitigate N fluxes from coastal watersheds are often guided by models that predict changes in N loads as a function of changes in land use, management practices, and climate. However, relatively little is known on the impacts of such changes on the relative fractions of different N forms. We leveraged a long-term dataset of N loads from over 100 river stations to investigate how the NO_3^- fraction, that is, the ratio of NO_3^- to total N (NO_3^-/TN), changes as a function of spatio-temporal changes in TN loads in the Chesapeake Bay watershed. We built a hierarchical model that separates the response of NO_3^- to changes in TN load occurring at different scales: *Across* river stations, where differences in TN loads are largely driven by spatial differences in anthropogenic inputs, and *within* stations, where inter-annual variability in hydrology is a key driver of changes in TN loads. Results suggest that while increases in TN loads resulting from changes in anthropogenic inputs lead to an increase in the NO_3^- fraction, a decrease in the NO_3^- fraction may occur when increases in TN loads are driven by increased streamflow. These results are especially relevant in watersheds that may experience changes in N loads due to both management decisions and climate-driven changes in hydrology.

(KEYWORDS: Chesapeake Bay; nitrogen loads; nitrogen speciation; hydrology; anthropogenic nitrogen inputs; hierarchical model.)

INTRODUCTION

Eutrophication due to excessive nutrient inputs is a common problem in aquatic ecosystems and nitrogen (N) inputs from anthropogenic sources are a key driver of water quality impairment in coastal systems (Howarth and Marino 2006; Conley et al. 2009). Efforts aimed at developing strategies to reduce N inputs delivered to coastal waters have been implemented in coastal systems worldwide (Boesch 2019). Such nutrient reduction plans are typically guided by empirical and/or mechanistic models that predict changes in watershed N export under a set of counterfactual management and climate scenarios (Stow et al. 2003; Shenk and Linker 2013; Scavia, Bertani, et al. 2017; Scavia, Kalcic, et al. 2017). These modeling tools are informed by decades of extensive research on the effects of changes in land use, management practices, local weather, and large-scale climatic patterns on the magnitude, timing, and spatio-temporal characteristics of watershed N loads

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(Vitousek et al. 1997; Schlesinger 2009; Gao and Guo 2014; Chanat and Yang 2018; Ator et al. 2019; Ballard et al. 2019). However, relatively less is known on the effects of such changes on N speciation, that is, the relative proportions of the different chemical forms of N that make up the overall N load exported from a watershed. Dissolved, particulate, organic, and inorganic N forms often originate from different sources in different portions, exhibit different levels of biogeochemical reactivity, and go through different dominant cycling and transport processes in terrestrial and aquatic environments (Hedin et al. 1995; Bernot and Dodds 2005; Alvarez-Cobelas et al. 2008). As a result, it is reasonable to hypothesize that they may respond differently to the changes in hydrological conditions, relative dominance of different biogeochemical processes, and overall N inputs to the landscape brought about by changes in land use, management actions, and climate. Understanding how the relative proportion of different N forms may vary in response to drivers that act as surrogates of anthropogenic and environmental change is particularly important because different N forms exhibit markedly different degrees of bioavailability and effectiveness in fueling algal growth and related eutrophication problems, such as hypoxia and harmful algal blooms (Seitzinger, Sanders, et al. 2002; Pehlivanoglu and Sedlak 2004; Bronk et al. 2007; Shenk et al. 2020).

Both local and large-scale studies show a generally consistent increase in the fraction of N load represented by dissolved inorganic forms, primarily NO_3^- and secondarily NH_4^+ and NO_2^-, in predominantly agricultural watersheds compared to more pristine regions characterized by lower anthropogenic N inputs (Perakis and Hedin 2002; Dodds 2003; Lehrter 2006; Scott et al. 2007; Sponseller et al. 2014). An increase in the NO_3^- fraction, that is, the ratio of NO_3^- to total N (NO_3^-/TN), is therefore generally expected as a result of increases in N loads driven, for example, by increased fertilizer application or a shift in dominance from forested to crop land uses. On the other hand, there is still substantial uncertainty in the relative response of different N forms to changes in N loads associated with changes in hydrology that may be brought about by different factors, such as shifts in climate conditions or changes in anthropogenic uses that significantly alter the hydrological cycle. Of the large number of process-based studies that have addressed the question of how N loads are expected to change as a result of different climate and hydrological conditions, relatively few have investigated the behavior of multiple N species and those who did reported contrasting results. For example, while some studies suggested that an increase in riverine N loads associated with climate-driven increases in precipitation and runoff would result in decreased NO_3^- fractions (Wang and Kalin 2018; Mehan et al. 2019), others reported an increase in the NO_3^- fraction (Park et al. 2013; Feng et al. 2015; Gabriel et al. 2016). On one hand, this lack of consensus may reflect the difficulty of generalizing the outcome of processes that are closely linked to site-specific attributes such as, among others, soil characteristics, topography, lithology, dominant land use types, hydrogeologic setting, local weather patterns, stream morphology, and lateral hydrologic connectivity. On the other hand, discrepancies in mechanistic model results are at least partly driven by substantial model structural uncertainty stemming from an imperfect knowledge of the biogeochemical mechanisms underlying N speciation and their mathematical representation, coupled with differences across modeling tools in the level of complexity, spatio-temporal resolution, quality and quantity of input datasets, and parameterization and calibration approaches.

Empirical analyses of observations from long-term monitoring programs can provide useful data-driven insight to inform assumptions, augment mechanistic formulations, and/or assess performance of process-based models especially with respect to outcomes characterized by relatively high mechanistic uncertainty. The Chesapeake Bay Program, a Federal-State partnership of six States (Virginia, Maryland, Pennsylvania, Delaware, West Virginia, and New York), the District of Columbia, and the Environmental Protection Agency representing the Federal Government with the objective of restoring the tidal waters and watershed of the Chesapeake (Linker et al. 2013), maintains a multi-decadal dataset of N loads estimated at over 100 nontidal riverine stations across the Bay watershed (USEPA 2004). Loads of NO_3^-, the dominant form of dissolved inorganic N, and of TN are estimated routinely, thereby providing an ideal dataset to investigate how the NO_3^- fraction changes over time and space as a function of changes in N loads. Understanding N speciation is particularly important to develop strategies that can effectively reduce hypoxia and maintain ecologically healthy dissolved oxygen concentrations in the deep waters of the Chesapeake because dissolved inorganic forms of N, primarily NO_3^- and NH_4^+, are estimated to be an order of magnitude more potent in generating bottom water hypoxia in the Bay than particulate refractory organic N (Cerco and Noel 2019). In addition to that, the decision of the Chesapeake Bay Program to defend the living resource-based tidal water quality standards from future climate risk explicitly calls for an improved understanding of how N speciation is expected to respond to climate-driven changes in hydrology in the Bay watershed (Linker et al. unpublished).

The overarching aim of this work is to investigate how the NO_3^- fraction changes as a function of spatiotemporal changes in riverine TN loads across the Chesapeake Bay watershed. To achieve this, we developed an empirical model that relates changes in annual NO_3^- loads to changes in annual TN loads estimated at nontidal riverine stations. More specifically, we address the question of whether the NO_3^- fraction is expected to respond similarly to changes in TN loads associated with increased anthropogenic N inputs between stations as opposed to changes in TN loads largely driven by varying hydrology within stations. Although numerous factors contribute to influence the spatial and temporal variability in riverine TN loads observed in a watershed, hydrology is generally found to be the dominant driver of interannual variability, while differing levels of anthropogenic N inputs associated with different dominant land uses and management practices are usually the strongest predictor of spatial variability (Basu et al. 2010; Sinha and Michalak 2016). We use a hierarchical model approach to simultaneously model and separate the response of NO_3^- to changes in TN load occurring at different scales in the watershed: *Across monitoring stations*, where differences in TN loads are assumed to be primarily driven by spatial differences in land use and average anthropogenic N inputs, and *within monitoring stations*, where interannual variability in hydrology is assumed to be the dominant driver of changes in TN loads. Hierarchical models are especially well suited to model cross-scale data that are structured into groups, such as samples collected at different monitoring stations, and they offer several benefits, including the ability to: (1) simultaneously model variation at the individual data level and at the group level, thereby assessing the response of individuals within groups and of the population as a whole, (2) address violations of the least squares assumption of independence arising from the inherent correlation of observations belonging to the same group, (3) improve estimates of model coefficients for groups with lower sample size and/or higher variability by "borrowing strength" from groups with larger sample size and higher strength of information, (4) account for and propagate different sources of uncertainty across the levels of the model hierarchy, and (5) incorporate predictors that act at different organizational levels of the hierarchy, thereby accounting for cross-scale interactions among variables that act at different spatial and/or temporal scales (Gelman and Hill 2007; Qian and Shen 2007; Cressie et al. 2009; Stow et al. 2009; Qian et al. 2010; Soranno et al. 2014). By explicitly separating the spatial and temporal components of the NO_3^- response to changes in TN loads across a watershed, the resulting empirical model can (1) provide insight into how the NO_3^- fraction may change as a result of changes in the main drivers that dominate each of those components, (2) serve as an empirical augmentation of watershed models (e.g., Shenk and Linker 2013) whose calibration and predictions are primarily focused on TN, and (3) serve as an additional validation tool for mechanistic models that predict changes in the relative proportion of NO_3^- over other N forms as a function of different underlying processes.

MATERIALS AND METHODS

Annual NO_3^- and TN loads estimated at 101 Chesapeake Bay Nontidal Network stations (Figure 1; Table 1) over the period 1985–2016 through the Weighted Regression on Time, Discharge, and Season (WRTDS) method (Hirsch et al. 2010) were obtained from the United States Geological Survey (USGS) (Moyer et al. 2017) and were expressed in units of kg/ha (also referred to as yields) after normalization by each station's drainage area. Briefly, WRTDS is a statistical technique that estimates a complete daily record of constituent concentrations and loads based on an incomplete dataset of (infrequently) observed constituent concentrations and a complete record of daily discharges (Hirsch et al. 2010). The USGS uses the WRTDS method to estimate constituent loads at the Chesapeake Bay Nontidal Network stations with at least five years of monitoring data, whereby in each year a minimum of 20 constituent concentration samples are generally collected (12 monthly samples + 8 storm-event samples) (Chanat et al. 2016). Loads of NO_3^- represent the sum of NO_3^- and NO_2^-, although the latter generally represents a negligible fraction compared to the former (Meybeck 1982).

Annual loads were available over the full period of record (32 years) at 39 stations, while at other stations the length of the period of record ranged between 5 and 31 years, resulting in a total of 2013 data points. The statistical analyses described below were performed both retaining all stations and excluding stations with <10 years of data, and because results did not differ significantly, we report results of analyses performed on the full dataset.

To explicitly model the spatial (across stations) and temporal (across years, within stations) components of the NO_3^- response to changes in TN load, we built a hierarchical model that quantifies the relationship between annual NO_3^- and TN loads (temporal component), where the coefficients that characterize that relationship are allowed to vary hierarchically across stations (spatial component). The hierarchical formulation accounts for the fact

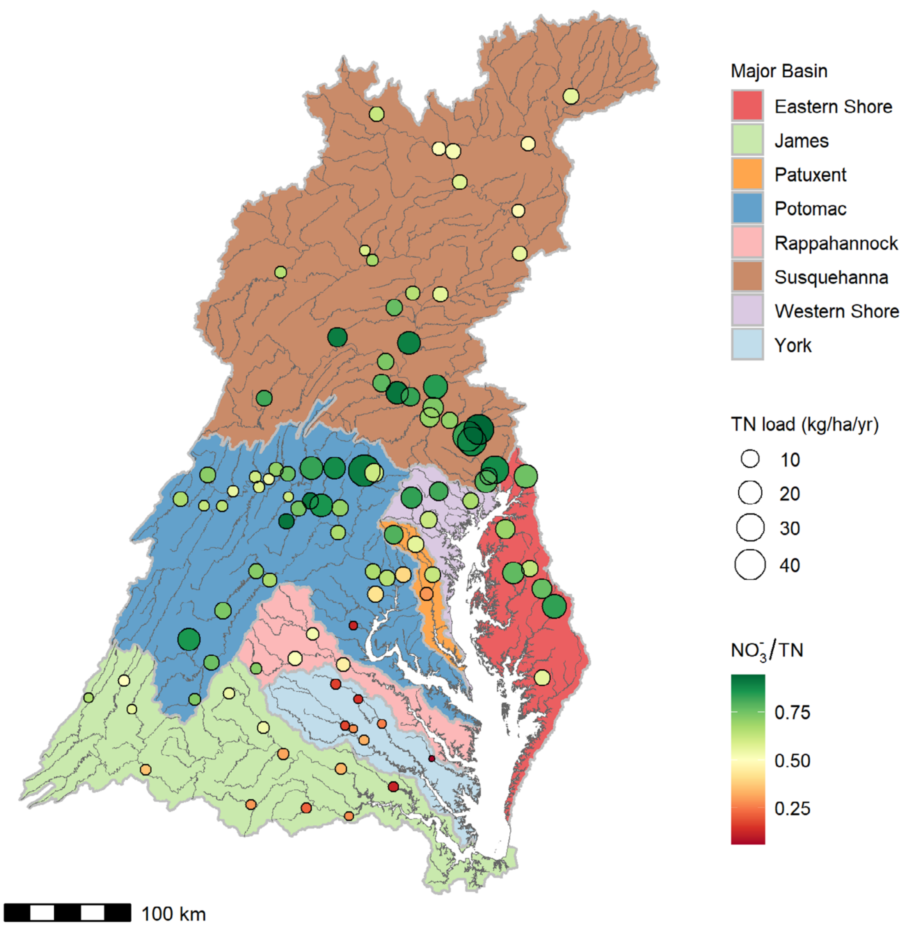

FIGURE 1. Map of 101 Chesapeake Bay Nontidal Network stations considered in this study. Circle size is proportional to the long-term total nitrogen (TN) load estimated at each station, while color indicates the long-term NO_3^- fraction estimated at each station from Weighted Regression on Time, Discharge, and Season loads.

that annual loads belong to different monitoring stations by entailing two levels, an Individual Level (where individual data = annual NO_3^- loads at each station) and a Group Level (where groups are represented by stations). At the Individual Level, each observation of the response variable (annual NO_3^- load in year i at station j, $NO_{3i,j}$) is modeled as arising from a normal distribution with mean $\hat{y}_{i,j}$ and standard deviation σ_j (Equation 1), where $\hat{y}_{i,j}$ represents the mean deterministic model prediction for the individual observation $NO_{3i,j}$ as a function of the Individual Level predictor $TN_{i,j}$ (Equation 2). Based on preliminary analyses of residuals, we found that a nonlinear formulation of the functional relationship between annual NO_3^- and TN loads at each station provided a better fit to the data, especially near the edges of the range of observed TN loads (Figure S1), as is frequently the case with water quality variables (Bolker et al. 2013; Filstrup et al. 2014). We also found that common transformations of the response and predictor variables, such as log transformations, failed to appropriately address the nonlinearity of the relationship. After testing different nonlinear deterministic functions (Bolker 2008), a modification of a sigmoidal model commonly used in ecology, the Holling Type III functional response equation (Equation 2), was found to provide the best compromise between model performance and parsimony (i.e., number of parameters to be estimated by the model). The deterministic form of the model is thus a nonlinear regression between annual NO_3^- loads and annual TN loads at each station. At the Group Level, the two parameters (α and β) that quantify the functional relationship between $NO_{3i,j}$ and $TN_{i,j}$ are allowed to vary across stations. Specifically, instead of estimating one single value of α and β for the whole dataset, as is typically done in classical regression, different α_j and β_j values are estimated for each station j and these station-specific α_j and β_j values are themselves modeled as random variables arising from probability distributions. As mentioned above, the hierarchical structure of the model allows for the incorporation of Group Level covariates that may help to explain the spatial (i.e., between stations) variation in model

TABLE 1. Summary statistics of the distributions of select characteristics across the 101 stations considered in this study. The variables Cropland, Pasture, Developed, and Forested represent the fraction of a station's drainage area occupied by the corresponding land use category. Average annual TN loads and NO_3^- fractions were calculated by averaging across individual years at each station, with the total number of years at each station varying between 5 and 32. Q1 and Q3 are the first and third quartile of each variable's distribution, respectively. Distributions are representative of the characteristics of the stations considered in this study and not the whole watershed.

	Min	Q1	Median	Mean	Q3	Max
Drainage area (km^2)	2.6	220.2	536.1	4,275.7	1,958.0	70,188.7
Cropland (%)	0	7	15	18	23	72
Pasture (%)	0	4	7	7	9	21
Developed (%)	1	5	8	12	14	64
Forested (%)	10	38	60	55	71	91
Average annual TN load (kg/ha/year)	1.2	3.0	6.6	8.8	11.4	43.4
Average annual NO_3^- fraction	0.06	0.53	0.65	0.62	0.76	0.94

coefficients α_j and β_j. We then modeled both sets of parameters as arising from a multivariate normal distribution whose respective means are estimated as a linear function of the long-term average TN load estimated at each station ($\overline{\mathrm{TN}}_j$) (Equations 3 and 4). The inclusion of the station-specific long-term average TN load as a Group Level covariate serves two purposes. From a conceptual perspective, the long-term average load at each station can be viewed as a surrogate for the spatial signature of the integrated effects of land use, management practices, watershed characteristics, and land-based N inputs and we are therefore interested in quantifying its effect on the spatial variability in the model coefficients α_j and β_j. From a hierarchical modeling perspective, because we expect a positive correlation between the station-specific coefficients α_j and β_j and the Individual Level predictor $\mathrm{TN}_{i,j}$, the inclusion of the average of $\mathrm{TN}_{i,j}$ calculated at each station (i.e., $\overline{\mathrm{TN}}_j$) as a Group Level predictor is necessary to appropriately account for that correlation and avoid violations of Gauss–Markov assumptions (Bafumi and Gelman 2006; Gelman et al. 2008). Visual inspection of plots of residuals vs. fitted values indicated violation of the variance homogeneity assumption, with the Individual Level residual variance differing across stations and increasing with increasing values of $\overline{\mathrm{TN}}_j$. To appropriately account for this behavior, we allowed the Individual Level standard deviation to vary across stations and modeled it with the log-normal distribution defined by Equation (5), where the mean of the distribution is a function of $\overline{\mathrm{TN}}_j$ and the parameters γ, δ, and σ_ϵ are estimated by the model (Gelman and Hill 2007; Shor et al. 2007; Leckie et al. 2014).

Individual Level

$$\mathrm{NO}_{3i,j} \sim N\left(\hat{y}_{i,j}, \sigma_j^2\right), \quad (1)$$

$$\hat{y}_{i,j} = \frac{\alpha_j \times \mathrm{TN}_{i,j}}{\sqrt{\beta_j^2 + \mathrm{TN}_{i,j}^2}}, \quad (2)$$

Group Level

$$\begin{pmatrix} \alpha_j \\ \beta_j \end{pmatrix} \sim \mathrm{MVN}\left(\begin{pmatrix} a_0 + a_1 \times \overline{\mathrm{TN}}_j \\ b_0 + b_1 \times \overline{\mathrm{TN}}_j \end{pmatrix}, \Sigma\right), \quad (3)$$

$$\Sigma = \begin{pmatrix} \sigma_\alpha & 0 \\ 0 & \sigma_\beta \end{pmatrix} \Omega \begin{pmatrix} \sigma_\alpha & 0 \\ 0 & \sigma_\beta \end{pmatrix}, \quad (4)$$

$$\sigma_j \sim \mathrm{LN}\left(\gamma + \delta \times \log(\overline{\mathrm{TN}}_j)\right), \sigma_\varepsilon^2), \quad (5)$$

where $\mathrm{NO}_{3i,j}$: NO_3^- load (kg/ha) in year i at station j; $\hat{y}_{i,j}$: mean deterministic model prediction for $\mathrm{NO}_{3i,j}$; $\mathrm{TN}_{i,j}$: TN load (kg/ha) in year i at station j; $\overline{\mathrm{TN}}_j$: long-term average TN load (kg/ha) at station j; α_j, β_j: station-specific coefficients quantifying the nonlinear relationship between NO_3^- and TN at each station; a_0, a_1, b_0, b_1: coefficients quantifying the relationship between station-specific model coefficients and $\overline{\mathrm{TN}}_j$; σ_j: within-station residual standard deviations after accounting for the effect of $\mathrm{TN}_{i,j}$; Σ: variance-covariance matrix for the station-specific coefficients α_j and β_j; Ω: correlation matrix for the station-specific coefficients α_j and β_j; σ_α, σ_β: standard deviations of station-specific coefficients after accounting for the effect of $\overline{\mathrm{TN}}_j$; γ, δ: coefficients quantifying the heteroscedastic structure of the Individual Level standard deviations (σ_j); σ_ϵ: standard deviation quantifying the variability of the Individual Level error (σ_j) across stations; N, MVN, LN: Normal, Multivariate Normal, and Log-normal distribution, respectively.

We used diffuse or weakly informative priors for all parameters: a_0, a_1, b_0, b_1, γ, δ ~ Normal(0, 10); σ_α, σ_β, σ_ϵ ~ Uniform(0, 100). The correlation matrix Ω was given a Lewandowski, Kurowicka, and Joe (LKJ) prior: Ω ~ LKJcorr(2) (Lewandowski et al. 2009; Stan Development Team 2019b). Model parameters' posterior distributions were estimated within a Bayesian framework using a Markov Chain Monte Carlo (MCMC) algorithm implemented in the software STAN (Carpenter et al. 2017) interfaced with R (R Core Team 2018) through the R package rstan (Stan Development Team 2019a). We ran four parallel MCMC chains with 3,000 iterations each after a warm-up period of 1,000 iterations. We considered the chains to have converged when < 1.1 for all model parameters, where for each parameter represents the ratio between the parameter's variance estimated by pooling all chains together and the average of that parameter's individual within-chain variances (Stan Development Team 2019c). We assessed model fit by computing the fraction of variance in the observations explained at each level (Individual and Group) of the model (Gelman and Pardoe 2006; Wagner et al. 2011) and by visually assessing the distribution of the posterior predictive p-values estimated for each individual observation. Posterior predictive p-values can be defined as the tail-area probability of each observation under the posterior predictive distribution estimated by the model for that observation (Meng 1994; Gronewold et al. 2009). In other words, an observation's posterior predictive p-value represents the probability that the model-predicted response is equal to or higher than the observation. Posterior predictive p-values were estimated for each observation $NO_{3i,j}$ by calculating the fraction of the corresponding posterior predictive distribution estimated by the model that exceeds that observation. A distribution of posterior p-values close to uniform indicates a good fit of the posterior predictive distribution to the observed data (Gelman et al. 2013). A leave-one-station-out cross-validation was performed to assess model performance when predicting at stations not included in the training dataset. At each step of the cross-validation procedure, one station was removed from the calibration dataset and the model calibrated to the remaining stations was used to predict NO_3^- loads at the excluded station.

RESULTS

The nontidal riverine stations considered in this study are spread throughout the Chesapeake Bay watershed and span a broad range of hydrologic and land use characteristics, with drainage areas ranging from 2.6 to 70,188.7 km^2 and upstream land use ranging from up to 72% cropland to over 90% forested (Figure 1; Table 1). As a result of these marked differences in land use characteristics, the long-term average annual TN load also varies substantially across stations, from a minimum of 1 kg/ha/year to a maximum of 43 kg/ha/year (Table 1). As expected, the spatial variability in average TN load follows spatial patterns in land use relatively closely, with higher TN loads generally found at stations characterized by higher fractions of anthropogenically impacted land uses, such as crop or developed urban land uses, in the upstream catchments (Figure 2a). The average NO_3^- fraction also exhibits considerable spatial variability across stations (Figure 1; Table 1) and is positively correlated with the average long-term TN load estimated at each station, that is, stations with higher TN loads (and higher fractions of anthropogenically impacted land uses) tend to have higher NO_3^- fractions (Figures 1 and 2b).

However, when looking at inter-annual variability in the NO_3^- fraction within each station, that relationship is often reversed, with years characterized by higher TN loads generally exhibiting lower NO_3^- fractions (Figure 3). A hierarchical model with different coefficients across stations captures this dual behavior by separating within- and across-station variability (Figure 3).

Posterior distributions of all model parameters are substantially narrower than their corresponding priors, indicating that the amount of information in the data was sufficient to update the parameters' distributions and priors exerted minimal influence on posterior parameter estimates (Figure S2). At the Individual Level, that is, when considering all 2013 annual data points across all 101 stations, the model explains 99% of the variation in $NO_{3i,j}$ (Figure 4), with a root mean square error (RMSE) of 0.48 kg/ha and a mean absolute error (MAE) of 0.22 kg/ha. An ordinary least squares regression that pools observations from different stations together (complete pooling) performs similarly in terms of amount of variation explained in the response variable ($R^2 = 97\%$) but underperforms in terms of RMSE (1.14 kg/ha) and MAE (0.80 kg/ha). More importantly, a regression model that pools all observations together predicts a positive relationship between the NO_3^- fraction and TN loads but fails to capture the decrease in the NO_3^- fraction observed with increasing TN loads as a result of inter-annual variability within stations (Figure 3).

There is substantial spatial (across-stations) variability in the parameters that characterize the relationship between NO_3^- and TN and both parameters exhibit a positive relationship with the long-term

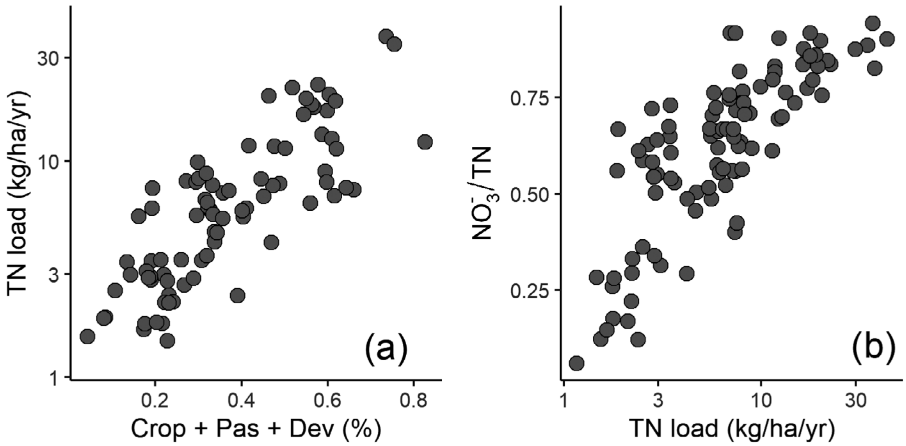

FIGURE 2. Relationship between (a) long-term average TN load estimated at each of 101 riverine stations in the Chesapeake Bay watershed and the fraction of upstream land occupied by crop, pasture, and developed land uses and (b) NO_3^- fraction and long-term average TN load.

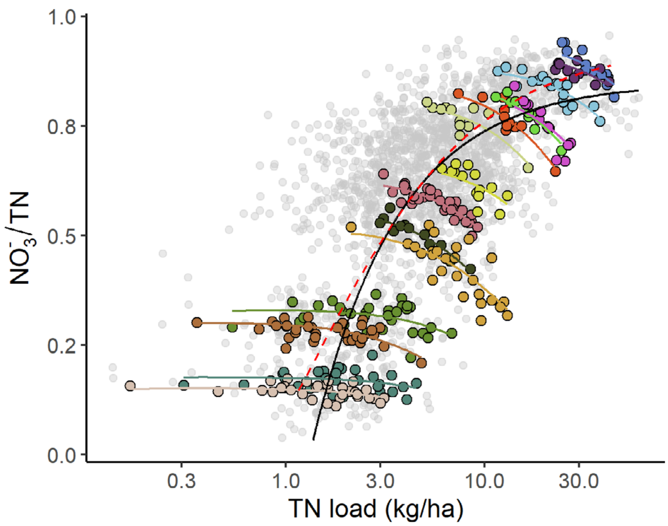

FIGURE 3. Relationship between annual NO_3^- fraction and log-transformed annual TN load estimated at 101 riverine stations in the Chesapeake Bay watershed. Different colors represent different stations and show the generally negative relationship between annual NO_3^- fraction and TN load within each individual station. Only a subset of the stations was highlighted with colors different from gray to prevent excessive cluttering and aid interpretation. Colored lines represent predicted NO_3^- fraction values from station-specific regressions obtained through hierarchical modeling, while the solid black line represents NO_3^- fraction values predicted when fitting a least-squares regression that pools all observations together. The red dashed line is obtained by replacing $TN_{i,j}$ with the long-term average TN load at each station ($\overline{TN}_j$) in Equation (2) of the hierarchical model, thereby estimating how the long-term average NO_3^- fraction is predicted to vary after removing inter-annual variability in TN loads. Note that a decrease in the NO_3^- fraction also occurs at stations characterized by relatively low TN loads, although less evident due to the generally lower NO_3^- fraction values and also as a result of the log transformation stretching the range of smaller values on the x axis.

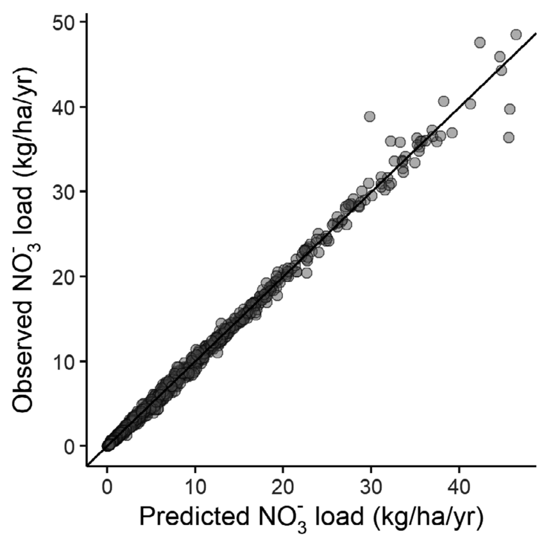

FIGURE 4. Observed vs. model-predicted annual NO_3^- loads at 101 nontidal riverine stations in the Chesapeake Bay watershed. The 1:1 line is provided for reference. See Supporting Information for a figure of observed vs. model-predicted annual NO_3^- fractions (Figure S4).

average TN load, as indicated by the posterior mean values of the two Group Level slope parameters a_1 and b_1, whose 95% credible intervals are above zero (Table 2). Specifically, long-term average TN explains 88% and 84% of the across-station (Group Level) variation in the parameters α_j and β_j, respectively. A histogram of marginal posterior predictive p-values exhibits relatively minor deviations from a uniform distribution between 0 and 1 (Figure S3). Because each posterior predictive p-value quantifies the portion of the model-predicted probability distribution

TABLE 2. Model-estimated posterior parameter means and standard deviations.

Parameter	Units	Posterior mean	Posterior SD
a_0	kg/ha	−2.11	1.52
a_1	(kg/ha)/(kg/ha)	2.80	0.17
b_0	kg/ha	4.09	2.01
b_1	(kg/ha)/(kg/ha)	2.84	0.22
γ	kg/ha	−3.23	0.13
δ	(kg/ha)/log(kg/ha)	0.94	0.06
σ_ϵ	kg/ha	0.48	0.04
σ_α	kg/ha	8.41	0.97
σ_β	kg/ha	10.24	1.29

that exceeds the corresponding observation, a tendency of p-values to exhibit values close to zero or one would indicate that model-predicted uncertainty intervals tend to be narrower than expected, while a relatively uniform distribution of p-values provides support for the ability of the model to appropriately characterize predictive uncertainty (Gronewold et al. 2009; Obenour et al. 2014). Station-specific regressions, whose coefficients depend on a station's long-term TN load through Equation (3), can be used to predict annual NO_3^- fractions as a function of annual TN loads at each station. Furthermore, the Group Level relationship between the station-specific coefficients (α_j and β_j) and the corresponding long-term average TN loads allows for the estimation of new values of α_j and β_j for stations not included in the dataset used to fit the model, provided that the long-term average TN load of those stations is known. To gain an approximate indication of how the model would perform when predicting at single stations excluded from the calibration dataset, results of leave-one-station-out cross-validation can be compared to the performance of the full model. Our cross-validation results suggest only a marginal decrease in model predictive performance compared to the full model (CV-R^2 = 98%, CV-RMSE = 1.05 kg/ha, MAE = 0.75 kg/ha). When used in cross-validation mode, the model exhibits similar predictive performance to the completely pooled regression, while still retaining the ability to model variability within and across stations separately.

DISCUSSION

Our empirical approach found evidence of an opposite-direction response of the NO_3^- fraction to changes in TN loads depending on whether the TN changes were governed by spatial (i.e., management/land use) or temporal (i.e., hydrology) drivers. At the spatial scale (across riverine stations), we found an increase in the NO_3^- fraction with increasing TN loads (Figures 2b and 3). A simple linear regression of station-specific long-term average TN loads as a function of the total fraction of upstream land occupied by land uses typically characterized by high N inputs (cropland, pasture, and developed) explains 66% of the variability in TN loads in the log space (Figure 2a), confirming that land use is a major driver of the observed spatial differences in TN loads. The results agree with extensive literature supporting widespread observations that an increase in the relative proportion of NO_3^- is associated with higher TN loads resulting from increased anthropogenic N inputs (Seitzinger, Kroeze, et al. 2002; Pellerin et al. 2006; Stanley and Maxted 2008). However, when changes in hydrology are a major driver of variability in TN loads, as is generally the case when looking at inter-annual variability within stations, the NO_3^- fraction tends to decrease as TN loads increase (Figure 3). A similar decrease in the relative contribution of NO_3^- and a corresponding increase in the fraction of particulate and dissolved organic N forms with hydrology-driven increases in N loads has often been reported in watersheds within and outside the Chesapeake Bay both at the individual storm event scale and at intra- and inter-annual time scales (Correll et al. 1999a; Gao et al. 2004; Kato et al. 2009; Inamdar et al. 2015). At the event scale, when stream discharge increases due to precipitation events, a shift from NO_3^--rich groundwater to subsurface and overland runoff as the dominant sources of streamflow may in some cases result in a net dilution effect on NO_3^- concentrations, coupled with the mobilization of relatively larger amounts of dissolved and particulate organic N from in- and near-stream sources, such as riparian soils, upper soil horizons, and eroded or re-suspended streambed and bank sediments (Correll et al. 1999b; Kaushal and Lewis 2003; Martin and Harrison 2011; Duncan et al. 2017). Such shifts in the composition of the N load observed at the scale of individual storm events may ultimately result in relatively lower NO_3^- fractions in wetter years compared to drier years (Correll et al. 1999a; Lehrter 2006; Rose et al. 2018). The occurrence of this type of response is dependent on complex interactions among several factors such as dominant land use, soil erodibility and organic matter content, magnitude, frequency and seasonal timing of storm events, occurrence and duration of dry–wet cycles, rates of accumulation of organic and inorganic N stores in the soil, and spatial distribution of those stores in the watershed (Lehrter 2006; Causse et al. 2015; Rose et al. 2018). Disentangling the underlying mechanisms that contribute to produce the patterns emerging from our analysis is beyond the scope of this work and would benefit from a combination of process-based studies and empirical analyses of load dynamics at finer temporal scales than inter-annual (Burns et al. 2019). Nonetheless, our results suggest that while increases in N load delivery resulting from potential increases in land uses characterized by high anthropogenic N inputs would be expected to lead to an increase in the relative fraction of NO_3^-, a decrease in the NO_3^- fraction could occur when increases in N delivery are driven primarily by hydroclimatic conditions. Examples of model-predicted changes in the NO_3^- fraction as a function of changes in TN loads primarily driven by hydrology (estimated using station-specific regressions such as those indicated by different colors in Figure 3) vs. N inputs (estimated using the regression line based on long-term average loads and indicated with a red dashed line in Figure 3) are provided in Table S1.

The findings may have direct implications in the Chesapeake Bay, where an overall increase in precipitation and streamflow is estimated as a result of climate change and was found in long-term observed data (Groisman et al. 2004; Najjar et al. 2010; Rice and Jastram 2015; Rice et al. 2017). A wetter watershed is in turn expected to increase the estimated delivery of N loads to the tidal Chesapeake (Chang et al. 2001; Sinha et al. 2017; Bhatt et al. unpublished). Although a substantial amount of that increase is expected to be in the form of NO_3^-, which is the dominant N form in several regions of the watershed (Figure 1), our results suggest that the fraction of NO_3^- may decrease relative to that of particulate and organic N forms under wetter conditions.

A decrease in the relative proportion of more reactive and readily bioavailable forms (NO_3^-) and a subsequent increase in the fraction of more refractory organic and particulate N would have potential ecological and water quality implications for streams, rivers, and ultimately the tidal waters of the Bay (Lewis et al. 2011; Paerl et al. 2014). In this regard, given the ecological importance of the stoichiometry of different N forms not only with respect to each other but also with respect to other algal nutrients (e.g., phosphorus and silica), the modeling approach presented here could be extended in the future to characterize the relative behavior of algal nutrients other than N with respect to changes in watershed inputs and hydrology (Viaroli et al. 2018; Vybernaite-Lubiene et al. 2018).

It is important to acknowledge that this empirical approach has limitations. Our model does not address the potential influence of confounding factors that act at different spatial and temporal scales and that most likely impact the N loads ultimately observed at the monitoring stations, such as long-term changes in land use and management practices, watershed characteristics, soil hydraulic properties, geologic setting, topography, in-stream water residence and travel time, anthropogenic water uses, etc. For example, stations where management actions have resulted in sustained decreases in N inputs over time are expected to respond with a corresponding long-term gradual decrease in the NO_3^- fraction that may partially confound the negative relationship found between the NO_3^- fraction and TN loads over time. To address this, the current approach could be refined in the future by removing potential long-term trends in the NO_3^- fraction within stations or by including a time-varying predictor in the model that captures long-term changes in land use and/or management at each station. In addition, the model currently does not address the fact that nested watersheds may exhibit nonindependent responses and although inspection of model residuals did not reveal any remaining spatial patterns, future efforts may include revising the model's formulation to explicitly model the spatial correlation structure inherent in the stream network. There are also inherent limitations and uncertainties associated with the WRTDS method that was used to estimate loads. Uncertainty in load estimates may arise and vary across stations and constituents as a function of factors including, among others, the number and frequency of water quality samples, length of the time series over which water quality samples are available, presence and duration of gaps in the sampling program, degree of bias in sampling frequency across seasons and/or flow event magnitudes, goodness of fit of the concentration–discharge relationships, etc. (Hirsch 2014; Lee et al. 2016). Future efforts could address some of these limitations for example by developing modeling approaches that leverage increasingly available high-frequency water quality data to improve load estimation accuracy (Burns et al. 2019) or by taking advantage of the flexible hierarchical formulation to incorporate additional station-level variables related to watershed characteristics that may capture some of the unexplained variability in the N speciation response.

It is also important to note that caution should be used when extrapolating observed watershed responses to inter-annual variability in hydrology to characterize expected responses to longer term, cumulative changes in hydrology. For example, antecedent flow conditions are known to influence the magnitude and characteristics of the pool of constituents stored in a watershed and available for downstream transport in a given year (Murphy et al. 2014; Outram et al. 2016). As a result, the biogeochemical response of a watershed to a wetter hydrology observed as part of inter-annual fluctuations in wet-dry conditions may differ from the cumulative effect of a sustained increase in wet conditions brought about by climate change, which may lead to long-term gradual changes in N sinks in the landscape or to shifts in the rates and relative importance of the different biogeochemical processes that affect speciation patterns in the watershed (Howarth et al. 2006; Greaver et al. 2016). In addition, there is still substantial uncertainty on the extent and type of adaptation measures expected in response to climate change and on how these potential changes in practices (e.g., changes in crop varieties, planting dates, timing, rate and mode of fertilizer application and irrigation) may ultimately affect the availability, transformation, and transport of different N species (Lal et al. 2011; Challinor et al. 2014). Addressing these uncertainties will most likely require the integration of results from multiple research approaches, including experimental manipulations, observational studies over long time scales and/or environmental gradients, and simulations of different climate and adaptation scenarios through mechanistic modeling (Dunne et al. 2004; Fukami and Wardle 2005; Thompson et al. 2013).

Despite the limitations of our modeling approach, we find a consistent negative response of the NO_3^- fraction to changes in N loads driven primarily by hydrology across the watershed, and our results are in agreement with some observational studies that have looked at the relative response of different N forms to changes in hydrology in the Chesapeake Bay watershed (Correll et al. 1999a; Inamdar et al. 2015). Although applied in the Chesapeake Bay watershed, our modeling approach is easily transferrable to other systems and results may be of particular relevance for watershed research, modeling, and management efforts, especially in coastal watersheds that are predicted to experience increases in N load delivery as a result of climate influences on precipitation and flow.

SUPPORTING INFORMATION

Additional supporting information may be found online under the Supporting Information tab for this article: Tables and figures with additional model details and results.

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AUTHORS' CONTRIBUTIONS

Isabella Bertani: Conceptualization; formal analysis; investigation; methodology; visualization; writing-original draft; writing-review & editing. **Gopal Bhatt:** Conceptualization; formal analysis; investigation; writing-review & editing. **Gary W. Shenk:** Conceptualization; formal analysis; investigation; supervision; writing-review & editing. **Lewis C. Linker:** Conceptualization; formal analysis; investigation; supervision; writing-review & editing.

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