Exploring Estuarine Nutrient Susceptibility

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The susceptibility of estuaries to nutrient loading is an important issue that cuts across a range of management needs. We used a theory-driven but data-tested simple model to assist classifying estuaries according to their susceptibility to nutrients. This simple nutrient-driven phytoplankton model is based on fundamental principles of mass balance and empirical response functions for a wide variety of estuaries in the United States. Phytoplankton production was assumed to be stoichiometrically proportional to nitrogen load and an introduced "efficiency factor" intended to capture the myriad processes involved in converting nitrogen load to algal production. A Markov Chain Monte Carlo algorithm of Bayesian inference was then employed for parameter estimation. The model performed remarkably well for chlorophyll estimates, and the predicted estimates of primary production, grazing, and sinking losses are consistent with measurements reported in the literature from a wide array of systems. Analysis of the efficiency factor suggests that estuaries with the ratio of river inflow to estuarine volume (Q/V) greater than 2.0 per year are less susceptible to nutrient loads, and those with Q/V between 0.3 and 2.0 per year are moderately susceptible. This simple model analysis provides a first-order screening tool for estuarine susceptibility classification.

Introduction

Eutrophication is a threat to coastal waters that is most often a result of society-mediated delivery of excess nutrients (1–4). This overenrichment can lead to serious and negative effects, such as harmful algal blooms, habitat loss, biodiversity changes, bottom oxygen depletion, and fishery loss (4, 5). Determining nutrient loading targets to ameliorate these impacts is ultimately an estuary-specific enterprise; however, there is also a growing need to understand more generally why some systems are more susceptible than others so that management guidance can be provided across systems (6).

The diversity of estuaries has made classification an important and difficult question for researchers and decision makers since the 1950s (7–9). The National Research Council proposed 12 factors that control estuarine responses, including physiographic setting, primary production, nutrient load, dilution, water residence time, stratification, hypsography, grazing of phytoplankton, suspended materials load and light extinction, denitrification, spatial and temporal distributions of nutrient inputs, and allochthonous organic matter inputs (4). Some recent U.S. classification efforts include a dissolved concentration potential (DCP) index (2), an Assessment of Estuarine Trophic Status (ASSETS) meth-

odology (10), the Coastal and Marine Ecological Classification Standard (CMECS) conceptual classification (11), stressor–response relationships developed over broad geographical scales (12), and a multivariate regression analysis as part of a synthesis to guide development of estuarine nutrient criteria (13). Similar efforts have also been developed for Peninsular Malaysia (14), Portugal, the EU Water Framework Directive (15), and England and Wales (16). A review of 26 classification schemes found that past systems focused mainly on terrestrial and aquatic systems and for specific regions and habitat types (9, 12). Kurtz et al. (6) reviewed dozens of classification schemes and concluded that the distinctions among approaches appear to be between hierarchical and nonhierarchical structures, data-driven and theory-driven, and functional vs physical structural and that some classifications combine two or more methods or combine classification with other tools like modeling.

Our approach is nonhierarchical, theory-driven but data-tested, and functional. It is a modeling approach to identify key features useful for classification. We use a simple model, based on fundamental principles of mass balance, empirical response functions, and an introduced estuarine efficiency term for a wide variety of estuaries to explore the basis for their susceptibility to nutrient loads, ultimately contributing to a classification scheme to guide nutrient control policies. As such, our aim is to develop a screening model for estuaries in general, not a prediction or forecasting model for specific estuaries.

Methods

Data Sources. Data for 99 estuaries are described in NEEA Estuaries Database (http://ian.umces.edu/neea) (3). For our analysis, we used 75 of those systems: 14 estuaries were dropped from our analysis based on extreme physical characteristics (e.g., very shallow, very deep, long residence time, or excessive loads). Ten others were dropped because early attempts with our model generated estimates of estuarine efficiency that were quite unrealistic (see below and Supporting Information). The remaining 75 estuaries (37 drowned rivers; 19 lagoons; 9 coastal bays; 10 fjords) still represent a diversity of depths (0.5 to 46 m), volumes (1.7×10^7 to 2.9×10^{10} m³), residence times (4 to 979 days), total nitrogen (TN) loads (1.3×10^4 to 5.3×10^7 kg/year), and summer surface chlorophyll concentrations (2.3 to 24.8 μg/L) (see Supporting Information). Freshwater discharge, salinity, and ocean boundary nitrogen concentrations were also obtained from this database; however, we found the reported values for ocean salinity were inconsistent with other published values for some subtributaries of the Chesapeake Bay. Accordingly, we recalculated water residence times (see below), based on updated salinity estimates for the Chester, Choptank, Rappahannock, Tangier/Pocomoke, and York river subestuaries from 1222, 713, 185, 1120, and 121 days to 276, 85, 108, 586, and 92 days, respectively.

Growing season chlorophyll a concentrations were derived from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) imagery reported monthly for 1997 to 2004 (http://geoportal.kgs.ku.edu/estuary/) (17). We used June–August averages for each of the 7 years. Annual average total nitrogen daily loads, based on the most recent SPARROW model updates (18), were provided by the U.S. Geological Survey (R. Alexander, personal communication). Because SPARROW is not well suited for the relatively flat Florida watersheds, we used NOAA-report fluxes reported on the NEEA Web site.

Model Development. While models can be useful tools for describing and predicting specific estuarine responses to

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changes in nutrient loads (e.g., refs *19−24*), they can also be useful in exploring more general responses to provide insights into what controls their susceptibility to eutrophication (*25, 26, 16, 27*). We developed a nutrient-driven phytoplankton model, simplified from previous studies on lakes and estuaries (*28−31*), that relates summer average phytoplankton biomass to spring TN daily loads and estuarine physical characteristics. Rather than model detailed nitrogen dynamics (including phytoplankton uptake and biogeochemical cycling), we modeled summer phytoplankton production as proportional to spring TN load, similar to earlier work simulating biological oxygen demand in the Gulf of Mexico and the Chesapeake Bay (*20, 22, 24*). The nitrogen loading rate was converted to phytoplankton carbon production by multiplying load by a factor encompassing the C:N ratio for nitrogen-limited production, the relationship between spring average daily and annual average daily load, and an "estuarine conversion efficiency factor" intended to capture processes converting nitrogen load to algal production. This is admittedly a very strong simplification, but it served the purpose of relating production to load and introducing the efficiency factor that became very useful in assessing estuarine susceptibility. We discuss this in detail below; however, we used this bulk property, the estuarine conversion efficiency, to calibrate the model and then to explore how it varied with various estuarine properties.

Phytoplankton losses are modeled as a first-order sinking rate and a zooplankton grazing term modeled as quadratic in phytoplankton biomass. This is similar to approaches used for zooplankton mortality (*32−34*) under the assumption that zooplankton abundance varies with phytoplankton abundance. Thus, the overall rate of change of mixed-layer phytoplankton carbon (B) is:

$$\frac{\mathrm{d}B}{\mathrm{d}t} = I_n - \frac{Q_{out}B}{V_1} - \nu'_{s1}B - LB^2 \tag{1}$$

$$I_n = \frac{TN_L}{V_1}\alpha = \frac{TN_R + TN_O}{V_1}\alpha \tag{2}$$

$$TN_O = Q_{in}N_O, \quad V_1 = z_fV, \quad \nu'_{s1} = \frac{\nu_s}{z_1} = \frac{\nu_s}{z_fz} \tag{3}$$

where B is phytoplankton biomass (g C/ m^3), I_n is phytoplankton production (g C/ m^3/day) derived from spring nutrient load (TN_L, g N/day) and calibration term (α, g C/g N); Q_{out} is the outflow to the ocean (m^3/day), ν'_{s1} is the sinking rate (1/day), ν_s is the sinking velocity (m/day), z_1 is the mixed layer depth (m), z is the estuary average depth (m), L is the grazing loss rate (m^3/g C/day), TN_L is the sum of TN_R (spring riverine TN load, g N/day) and TN_O (ocean nitrogen influx, g N/day) (ignoring atmospheric deposition sources and N fixation), N_O is the ocean nitrogen concentration (mg/L), Q_{in} is ocean inflow (m^3/day), V_1 is the mixed layer volume (m^3), and V is the estuary volume (m^3). The ratio of mixed layer depth to total depth z_f is 1.0 for well-mixed estuaries and assumed to be 0.5 for stratified estuaries. We assumed lagoons and all other estuaries with depth <3.0 m were well mixed and that all fjords were stratified.

The water residence time (WRT, day), Q_{out}, and Q_{in} can be calculated from average estuarine salinity (Sal_1), ocean boundary salinity (Sal_0), and river discharge (Q), all of which are in the NEEA Estuaries Database, and water and salt balances, as:

$$\begin{matrix} Q_{in}Sal_0 = Q_{out}Sal_1 \\ Q + Q_{in} = Q_{out} \end{matrix} \Rightarrow \begin{cases} Q_{out} = Q\dfrac{Sal_0}{Sal_0 - Sal_1} \\ Q_{in} = Q\dfrac{Sal_1}{Sal_0 - Sal_1} \end{cases} \tag{4}$$

WRT is defined as:

$$WRT = \frac{V}{Q_{out}} = \frac{V}{Q} \times \frac{Sal_0 - Sal_1}{Sal_0} \tag{5}$$

To explore the model's ability to reproduce summer phytoplankton concentrations, we solved eq 1 at steady state under the assumption that this will provide analytical power and adequate distinctions among estuaries (*35*). While phytoplankton biomass certainly varies over shorter periods and for most estuaries those differences are generally attenuated at annual scales (*36*), there remains sufficient discrimination among estuaries for this analysis. The steady-state solution, obtained by setting $(\mathrm{d}B)/(\mathrm{d}t) = 0$, is:

$$B = \frac{-(Q_{out} + V_1\nu'_{s1}) + \sqrt{(Q_{out} + V_1\nu'_{s1})^2 + 4I_nLV_1^2}}{2LV_1} \tag{6}$$

Parameter Estimation. Bayesian analysis has been increasingly applied in ecology (*37, 38*) because of its ability to handle uncertainty, incorporate prior information such as data and modeling experience, and develop probabilistic assessments to support decision making (*39*). Compared to traditional modeling approaches, Bayesian-estimated model parameters are embodied in the posterior probability density functions, which provide credible intervals for both parameter values and predicted states under various probability levels (*40*). See Supporting Information for details.

We used WinBUGS (version 1.4.3) (*41*), called from R (version 2.6.0; R2WinBUGS (version 2.1−8)) (*42*). With WinBUGS, we estimated a single value for parameters L, ν_s, and C:CHL across all estuaries and individual values of α for each estuary. Our previous modeling analysis revealed that the four parameters are correlated (see Supporting Information), so we used the following informative priors, based on literature information and experience (*39*), to provide reliable parameter estimates: $L \sim N(0.80, 0.25)I(0,)$; C:CHL $\sim N(50, 20)I(0,)$; $\nu_s \sim N(0.3, 0.10)I(0,)$. The numbers in the brackets represent the mean and the standard deviation and $I(0,)$ denotes censoring to eliminate negative values. We conducted a sensitivity analysis on the forms of the informative priors (see Supporting Information) and found they were relatively insensitive to the variance changes. We used a noninformative prior for α, assuming a normal distribution with unspecified mean and common variance, since we did not have credible prior information for this derived property (see Supporting Information) and we wanted to allow the algorithm maximum flexibility in its estimation.

Four goodness-of-fit measures were used to test model results between predicted and observed values: correlation coefficient, slope of the regression, coefficient of determination, R^2, and the root mean squared error (RMSE) (see Supporting Information).

Results

C:CHL and Chlorophyll Estimates. The model performed remarkably well, with a correlation between predicted and observed chlorophyll of 0.99 (Supporting Information). The slope of the regression fit is 0.96 with an intercept of 0.17 which is not significantly different from zero. R^2 is 0.99 with a RMSE of 0.50 and scale-independent RMSE of 0.051. We used a potential scale reduction factor, Rhat, to determine model convergence. Resulting Rhat values are all close to 1.0, indicating the model converges well (*42*). The mean and standard deviation of the posterior distribution for the carbon to chlorophyll ratio was 56 ± 10.6, well within the range reported in the literature (*43−47*). While these estimates are satisfying, it is important to also compare our calculated production and loss rates to observations because even simple models are capable of matching state variables based on erroneous, yet compensating, rate processes (e.g., ref *28*).
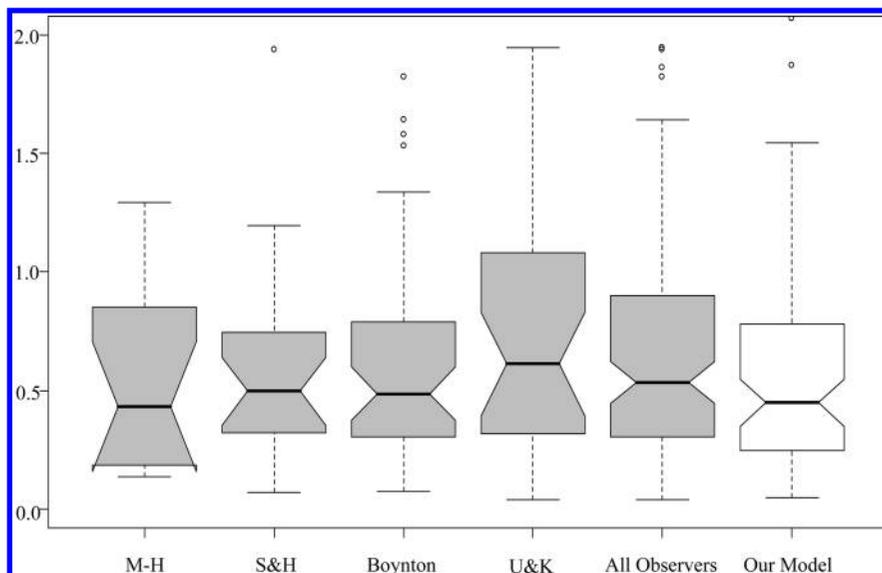
FIGURE 1. Frequency distribution of net primary production estimates for our study (75 estuaries) and that summarized in Montes-Hugol et al. (15 estuaries) (*51*), Smith and Hollibaugh (22 estuaries) (*50*), Boynton et al. (45 estuaries) (*48*), and Underwood and Kromkamp (30 estuaries) (*49*).

So we made those comparisons to ensure that this is not simply sophisticated curve-fitting.

Phytoplankton Primary Production. Model estimates for growing-season phytoplankton primary production ranged between 0.05 and 8.0 g C/m^2/day, with first, second, and third quartiles of 0.24, 0.45, and 0.78 g C/m^2/day. These estimates represent the central tendency of production for each estuary with distributions associated with α (eq 2). Thus, the overall distribution of the model production estimate is a mixture distribution. For comparison, we compiled summaries of phytoplankton primary production for 112 estuaries and coastal systems (*48−51*) and compared their distributions to our model. For cases where production estimates were reported as annual average daily rates, we assumed that 70% of the annual production occurs during the 7 month growing season. Comparing the notched box plots (Figure 1) illustrates that the distribution of our predictions are indistinguishable from those empirical estimates.

Grazing and Sinking Loss Rates. The mean and standard deviation of grazing and sinking parameters were 0.69 ± 0.27 m^3/g C/day for L and 0.21 ± 0.07 m/day for v_s, well within expected ranges for grazing (*33, 16*) and sinking (*46, 47*). In addition, grazing loss as a percent of primary production was 66 ± 18%, compared to 24 ± 15% for sedimentation, suggesting that grazing is often the main loss term. Estimates for the Strait of Georgia (*52*), Halifax Harbor (*53*), Chesapeake Bay (*54*), Mobile Bay (*55*), and Apalachicola Bay (*56*) all suggest that grazing was the primary factor controlling phytoplankton biomass. The consistency of the general patterns of model output and these observations is demonstrated by comparing the frequency distributions of model output to these field measurements across a wide array of systems (Figure 2 and Supporting Information). While some of our grazing estimates seem to be a bit higher than those reported in the literature, the overall comparison is quite good.

Estuarine Efficiency. The above comparisons of modeled and measured production, sinking, and grazing demonstrate that the model not only fits the observed phytoplankton chlorophyll concentration across this diverse set of estuaries but also fits key rate processes well. This lends credence to using the model to explore relative estuarine sensitivity through our estimates estuarine efficiency. The Bayesian estimated mean value of α that best fit chlorophyll observations ranged between 0.52 g C/g N and 159.5 g C/g N, with

the uncertainty around individual values relatively constant. Mean and standard deviation of the coefficients of variation were 17 ± 1%.

This calibration term, α, is composed of three factors: the nitrogen-limited C:N ratio for production, a factor relating average spring daily nutrient loads to annual average daily loads, and the estuarine efficiency factor. Because we want to explore the efficiency term, we need to factor out the other two; although it is important to note that the scaling factors influence the absolute value but not the patterns of α across estuaries.

The Redfield C:N molar ratio is often used for these types of estimates; however, recent evidence suggests that under nitrogen-limited conditions, carbon overconsumption (*57*) drives the C:N ratio higher. For our analysis, we used 12.7 (10.9 mass ratio), based on an average of 14 estimates reported in the literature (*58−64*). In most estuarine systems, average daily spring loads are considerably higher than the annual average. For our analysis, we assumed the average daily spring load was 2.0 times the annual average daily load. Thus, to estimate estuarine efficiency we divided α by 21.8 (10.9 × 2), producing efficiency terms between 0.02 and 7.34 (interquartile range: 0.34−2.28). Estuaries with efficiency terms greater than 1.0 can be considered "recyclers"; those below 1.0 can be considered "N sink" systems or highly flushed systems. This is discussed further below.

Discussion

The model reproduced summer chlorophyll concentrations as a function of total nitrogen load and the physical characteristics of the estuary for a wide range of estuarine types and conditions (Supporting Information). This was based on several simplifying assumptions, the most useful of which was the introduction of an estuarine efficiency term, representing the fraction of the spring nitrogen load converted to algal biomass. There are, of course, many processes that modulate that conversion and reduce overall conversion efficiency, including denitrification, delivery of unavailable nutrient forms, sediment burial, and rapid flushing compared to algal production. There are also processes that enable recycling of nitrogen and increase the conversion efficiency. Our analysis does not distinguish among those processes but rather explores their net effect. We explored how predicted estuarine efficiency, $\varepsilon = \alpha/21.8$, varied with different
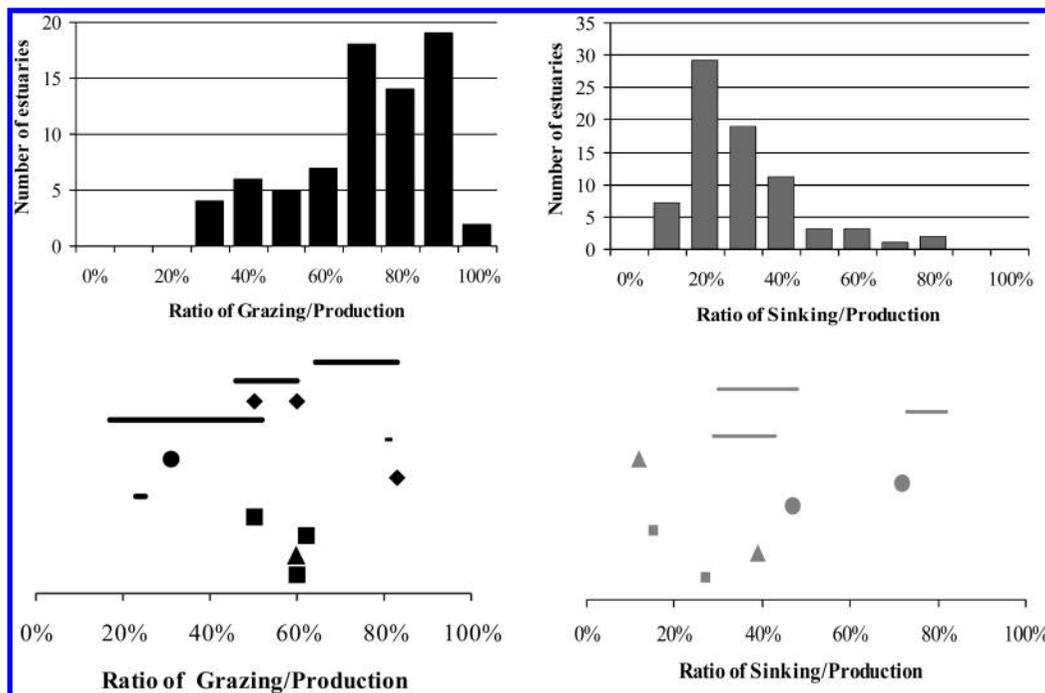
FIGURE 2. Frequency distribution of the ratio of sinking and grazing loss to production. Upper panels are model estimates; lower panels are literatures values (see Supporting Information).

estuarine properties and found the most useful relationship with the ratio of river discharge to estuarine volume (Q/V) (Figure 3, Supporting Information). Note that Q is the river discharge, not the sum of that discharge and ocean inflow, which is convenient because the latter is more difficult to estimate.

In this analysis, efficiency appeared to decrease roughly with the inverse square root of Q/V: $\varepsilon = 0.908(Q/V)^{-0.47}$ ($R^2 = 0.53$), where ε represents mean values arising from the 75 estimated normal distributions. This is logical because load generally increases with inflow (Q) and, for a given estuarine volume, one would expect the system to be less efficient in processing that load and, in fact, be overloaded for high values of Q. Conversely, for a given nutrient load, larger volumes should allow more time for biogeochemical processing and thus more efficient conversion.

The regression only explains a little over 50% of the variability and is thus not a strong predictor of individual efficiency or susceptibility. However, graphical inspection of ε vs Q/V estimates reveals an interesting pattern: a breakpoint a Q/V of 2.0 per year. All but one estuary with Q/V greater than 2.0 have efficiency factors less than 1, suggesting that nitrogen losses (e.g., denitrification, burial, delivery of refractory N) outweigh recycling rates in these "N sink" systems, and they are less susceptible to eutrophication. In contrast, all but four of the estuaries with Q/V less than 2.0 have efficiency factors greater than one and some as high as 7. These systems are more efficient recyclers and more susceptible to eutrophication. In addition, closer inspection of estuaries with Q/V values below 2.0 suggests that systems with Q/V between 0.3 and 2.0 have efficiency factors less than 3, i.e., moderate recyclers. Systems below 0.3 have indeterminate efficiency. Examining these relationships individually for lagoons, embayments, fjords, and river run estuaries (refer to the Supporting Information) demonstrates that almost all fjords are relatively sensitive to loads, whereas there is more variability in other types. This is similar to results from a multivariate regression analysis done for the same classes of estuaries (13).

Case Studies. We tested the general model against three case studies: Potomac River, Hudson River, and Apalachicola

Bay. Bennett et al. (65) found for the Potomac that chlorophyll a concentrations were low in July and August when average monthly discharge exceeded 200 m³/s, corresponding to Q/V over 0.97 year^{-1} based on a volume of 6.47×10^9 m³ (3). While seasonal peak concentrations occurred at discharges as high as 970 m³/s, sustained discharges greater than 1100 m³/s (the corresponding Q/V of 5.4) retarded development. Thus, for the Potomac River, sustained chlorophyll concentrations were consistently low for Q/V of 0.97 and 5.4 per year.

Howarth et al. (66) observed relatively high gross primary production (GPP) in Hudson River estuary only when river discharge at Green Island (representing 67% of total freshwater input) was less than 200 m³/s. This corresponds to a Q/V of 1.9, assuming a volume of 4.90×10^9 m³ (3). Observed GPP was less than 2.5 g C/m²/day when river discharge was over 200 m³/s. Using river discharge of 595 m³/s from the NEEA data set (3), we estimated production of 1.95 g C/m²/day and an efficiency term of 0.58 ± 0.11, indicating low susceptibility.

Apalachicola Bay is a fast-flushing estuary with a typical residence time of about 8 days and 66% of the annual nutrient input exported to the Gulf of Mexico (56). Our estimated efficiency was very low as 0.17 ± 0.03 with a Q/V ratio of 21.9 per year. The observed production from 1993 to 1996 ranged between 0.096 and 1.812 g C/m²/day; our estimate is 0.35 g C/m²/day.

Our analysis is based on a rather simple representation of relationships among nutrient load; phytoplankton growth, settling, and grazing; and basic physical estuarine properties. However, that simple formulation, embedded within a Bayesian estimation framework and employing an introduced term representing the nutrient conversion efficiency, was able to not only reproduce observed chlorophyll concentrations but to also mimic key relationships among rates of phytoplankton production, settling, and grazing loss. We demonstrated a relationship between this efficiency term (ε) and a flushing parameter, Q/V. While that relationship only explained a little over half of the variation in efficiency, graphical inspection suggests that estuaries with Q/V greater than about 2.0 per year should be less susceptible to nutrient
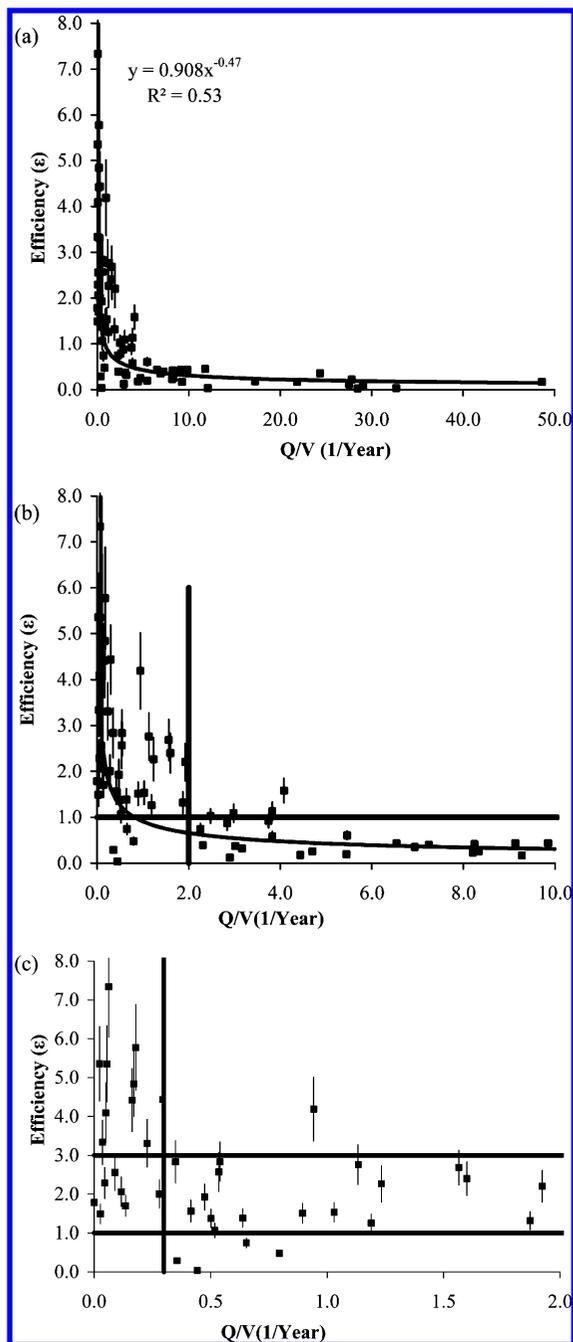
FIGURE 3. Relationship between nitrogen conversion efficiency (ε) and river discharge/estuarine volume (Q/V); three scales were used. Vertical error bars represent ± one standard deviation of the estimate. Vertical lines represent $Q/V = 2.0$ and 0.3. Horizontal lines represent efficiencies of 1 and 3.

loads and those with Q/V between 0.3 and 2.0 per year will be moderately susceptible. Little can be said generally for estuaries with Q/V less than 0.3 because ε varied between 1 and over 7.

While specific loading targets for individual estuaries will likely continue to be based on site-specific analysis, we suggest that a first-order screening tool based on the logical and rather classic property, Q/V, can help set priorities for analysis and perhaps form a basis for additional classification efforts on estuarine susceptibility.

Acknowledgments

Supporting Information Available

Text describing Bayesian analysis and literature values for comparison to modeled grazing and sedimentation; tables of estuarine characteristics, model results, and literature values used for comparison to modeled production; figures of estuarine characteristics, model results of predicted and observed chlorophyll concentration, relationships between estuarine efficiency, and different physical characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

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