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Use of geomorphic, hydrologic, and nitrogen mass balance data to model ecosystem nitrate retention in tidal freshwater wetlands

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Abstract

Geomorphic characteristics have been used as scaling parameters to predict water and other fluxes in many systems. In this study, we combined geomorphic analysis with in-situ mass balance studies of nitrate retention (NR) to evaluate which geomorphic scaling parameters best predicted NR in a tidal freshwater wetland ecosystem. Geomorphic characteristics were measured for 267 individual marshes that constitute the freshwater tidal wetland ecosystem of the Patuxent River, Maryland. Nitrate retention was determined from mass balance measurements conducted at the inlets of marshes of varying size (671, 5705, and 536 873 m^2) over a period of several years. Mass balance measurements indicate that NR is proportional to total water flux over the tidal cycle. Relationships between estimated tidal prism (total water volume) for spring tides and various geomorphic parameters (marsh area, total channel length, and inlet width) were defined and compared to field data. From these data, NR equations were determined for each geomorphic parameter, and used to estimate NR for all marshes in the ecosystem for a reference spring (high) tide. The resulting ecosystem NR estimates were evaluated for: (a) accuracy and completeness of geomorphic data, (b) relationship between the geomorphic parameters and hydrologic flux, and (c) the ability to adapt the geomorphic parameter to varying tidal conditions. This analysis indicated that inlet width data were the most complete and provided the best estimate of ecosystem nitrate retention. Predictions based on marsh area were significantly lower than the inlet width-based predictions. Cumulative probability distributions of nitrate retention indicate that the largest 3–4 % of the marshes retained half of the total nitrate for the ecosystem.

1 Introduction

Ecosystem functions, such as nitrate retention, are difficult to predict for entire ecosystems due to the complex interactions of linked biogeochemical and physical controls on ecosystem processes (Boyer et al., 2006; Seitzinger et al., 2006). The tidal freshwater wetland ecosystem, which is located at the interface between terrestrial and aquatic ecosystems, has been identified as an important site for nitrate retention (Simpson et al., 1983; Bowden et al., 1986, 1987). Evaluation of ecosystem nitrate retention and its distribution within this ecosystem is required to develop controls on eutrophication in coastal zones (Boyer et al., 2006; Howarth and Marino, 2006; Seitzinger et al., 2006).

Tidal freshwater wetlands (TFWs) often contain self-formed channel networks that govern water and solute fluxes into these systems (Myrick and Leopold, 1963; Rinaldo et al., 2004). Tidal channel networks are similar to fluvial networks; geomorphic relationships among stream order, length, basin area, and inlet width have been defined for both fluvial (Horton, 1945; Strahler, 1952; Shreve, 1967) and tidal channel networks (Rinaldo et al., 1999a; Marani et al., 2003). Geomorphic scaling parameters have been used to evaluate nitrogen (N) loads and processing in both terrestrial watersheds and tidal systems (e.g., Sferratore et al., 2005; Seitzinger et al., 2002). Previous research on N retention in TFW has identified marsh surfaces and near-surface environments as important sites for N processing (Bowden et al., 1986, 1987; Boynton et al., 2008). Normalized kinetic rate constants ($kg\,N\,yr^{-1}$) obtained from laboratory or field plot studies (e.g., Jenkins and Kemp, 1984; Caffrey et al., 1993; Joye and Paerl, 1994) have been used along with marsh surface area measurements and inundation times to upscale nitrogen retention for entire ecosystems (Boynton et al., 2008). Scaling nitrate retention to marsh surface area requires the following assumptions: marsh surface and near surface substrates are the dominant sites for nitrate retention; N processing rates are spatially homogeneous within marshes; and there is synchronous flooding of marsh surfaces of equal elevation. Several studies suggest that marsh materials are relatively homogeneous with little spatial variation in hydraulic properties (Harvey et al., 1987; Phemister, 2006) and nitrogen processing rates measured on marsh cores do not show systematic spatial variability (Cornwell et al., 1999; Merrill and Cornwell, 2000). Marsh-scale field studies of nitrate retention, however, indicate that in situ controls including inundation times may be complex and may involve parameters in addition to

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marsh surface area (e.g., Cornwell et al., 1999). Previous work on the Patuxent TFW ecosystem suggests that nitrate retention may be closely related to hydrologic flux in this system (Seldomridge and Prestegaard, 2011).

The purpose of this study is to evaluate geomorphic scaling parameters and to estimate total nitrate retention in TFW ecosystems. We obtained N retention data from field measurements of water fluxes and N species mass balance in marshes of varying sizes. These data were combined with geomorphic data for all marshes in the ecosystem to develop 3 equations (one for each geomorphic scaling parameter) to predict nitrate retention. Criteria used to evaluate geomorphic scaling parameters for nitrate retention are: (a) accuracy of measurement of each geomorphic feature, (b) relationship between each geomorphic parameter and hydrologic flux, and (c) the ability to adjust the geomorphic parameters to varying tidal stages and hydrologic fluxes.

2 Materials and methods

2.1 Study regions and approach

The Patuxent River watershed (2260 km^2) is located between Washington, DC and Baltimore, Maryland (Fig. 1). Land-uses in the basin include forest (63.5 %), agriculture (20.3 %), urban (15.7 %), and intertidal wetlands (0.4 %). Nitrate loads in the river have decreased in the past several decades largely due to reduction in point sources, but are still significantly higher than pristine watersheds (Fisher et al., 2006). The TFW ecosystem of the Patuxent River has been previously identified by Boynton et al. (2008); it extends approximately 25 river kilometers along the upper Patuxent River (from 39° 0′ N 76° 41′ W to 38° 43′ N 76° 41′ W). This ecosystem is composed of hundreds of individual marshes with well-defined tidal creeks and marsh basin areas. The individual marshes are contained within protected parkland, Patuxent Wetland Park and Jug Bay Wetlands Sanctuary (Fig. 1). Plant species that border tidal channels include: *Nuphar advena/leteum, Peltandra virginica, Polygonum sagittatum, Pontederia cordata*, and *Zizania aquatica*.

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Each individual tidal freshwater marsh in this ecosystem connects to the tidal Patuxent River through a well-defined inlet channel (Fig. 1b). Natural levees border the marsh boundary, which prevents direct overbank flooding from the Patuxent River into the adjacent marsh for most tidal stages. Interior marsh areas are flooded by water that enters through the tidal inlet, and then moves up the tidal network, where it floods onto marsh surfaces (Seldomridge, 2009). Fringing tidal wetlands without channel networks also border the Patuxent River, but these higher elevation marshes are inundated only during the upper 10 % of tidal or flood stages (high tide ± high Patuxent River flow). Due to this geomorphic arrangement of marshes along the tidal Patuxent River, water and solute fluxes can be measured at the inlet of each individual marsh. Nitrate retention calculated from fluxes (e.g. Nitrate flux in – Nitrate flux out) measured at channel inlets represent the consequences of net nitrate retention processes within each individual marsh system.

2.2 Geomorphic measurements and analysis

Marsh surface area, channel length, inlet channel width, and channel order were measured from high resolution air photos for every marsh and associated channel network in the tidal freshwater portion of the Patuxent River. Photo sources included: United States Department of Agriculture, 2006 and US Geological Survey, 2002–2005; 2007–2010. Measurements were made from autumn and winter photographs to minimize measurement error due to vegetation cover. Channel order was determined following the Horton (1945) numbering scheme. Measurements of inlet channel widths and lengths from air photos were compared with field measurements of the same features to determine accuracy of measurement and the resolution of measurement (e.g. smallest measurable channel width). Marsh surface area for each tidal basin was determined from vegetation patterns and associated elevation changes, which were often subtle on images of the smallest tidal marshes (highest elevation). Thus, a subset of the smallest marshes (with areas less than 55 m^2) could not accurately be determined. Operator error was determined from triplicate measurements

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of each geomorphic parameter. Operator error for channel width ranged from 1.72 % for the smallest measured channel (0.2 m) to 1.29 % for the largest measured channel (93.4 m); for channel length ranged from 1.5 % for the smallest channel (2.13 m) to 0.03 % for the largest channel (3773.1 m); and for marsh area ranged from 6.2 % for the smallest measured areas (225.6 m^2) to 0.15 % for the largest measured areas (675 611.9 m^2).

To investigate ecosystem geomorphic characteristics, we evaluated cumulative size distributions of the geomorphic data. A cumulative distribution is determined by sorting the data from largest to smallest and plotting the cumulative number against size of the geomorphic characteristic on a log–log plot. These distributions were evaluated to determine whether they exhibited power law behavior. The probability that an inlet width (W) greater than or equal to W_i can be written as:

$$P(W \geq W_i) \tag{1}$$

Data exhibit an inverse power law if $P(W \geq W_i) = \alpha W^{-\beta}$, where α and β are empirically-derived coefficient and exponent, respectively (Rinaldo et al., 1993; Scanlon et al., 2007). These distributions of geomorphic parameters were used to choose mass balance sampling locations, identify missing data, and assess the suitability of geomorphic parameters for modeling ecosystem nitrate retention.

2.3 Site selection for inlet cross section and nitrate mass balance measurements

Sites for field measurements of channel dimensions, water flux, and nitrogen mass balance measurements were chosen from the geomorphic probability distributions to represent a large range of tidal marsh sizes. Cross section measurements were made on 18 inlet channels, also chosen to represent the entire range of inlet channel sizes. Cross sections were measured at slack high tide of spring tidal stage conditions. Channel depth data were referenced to the high tide marsh platform elevations and tide gauge data.

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Nitrate retention measured by mass balance procedures may be sensitive to tidal water volumes, incoming nitrate concentration, and height of marsh vegetation; therefore, measurements of individual marshes were conducted during high (spring) tides during the same or sequential tidal cycles (Seldomridge, 2009). Mass balance measurements were made at the inlets of 3 individual marshes that were in close proximity to one another with areas of 671, 5705, and 536 873 m^2, respectively (Fig. 1c). Additional geomorphic characteristics for each mass balance measurement site are given in Table 1. Although mass balance measurements of nitrate retention were made for varying seasons and tides (from 2008–2011), only the data for flooding tides of spring tidal conditions in early autumn (20 September 2008, 1 October 2008 and 14 September 2011, 16 September 2011) were used in the ecosystem evaluation in this paper. In this system, the exotic submerged aquatic vegetation *Hydrilla verticillata* influences vegetative flow resistance during spring and summer months (Jenner and Prestegaard, in review), and thus affects water flux and nitrate retention. The autumn, spring tides represent a maximum water flux condition for which we examined geomorphic influences on nitrate retention.

2.4 Measurement of hydrologic flux during spring (high) tides

Hydrologic flux over a tidal cycle was determined by measuring tidal stage, associated channel cross sectional area, and velocity at time steps during tidal cycles. Tidal stage was measured at each inlet. These local tidal stage measurements were referenced to continuously monitored gauges at Jug Bay Wetlands Sanctuary (Maryland Department of Natural Resources Eyes on the Bay). Bankfull (maximum) channel cross sectional area was measured at slack high tides during spring tidal conditions. Velocity was measured at 10–12 intervals in the channel cross sections to determine discharge and average channel velocity (Q/A). Due to the rapid change in velocity with tidal stage, a relationship between average and maximum velocity was developed for each channel (Chen and Chiu, 2002), and from field measurements of maximum velocity, this relationship was used to determine average velocity for each time step (30 min).

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Discharge calculations for each time step were integrated to determine total water volume transported over the tidal cycle. A 5 % error was propagated through all discharge calculations; this was determined by considering operator error in cross sectional and velocity measurements (Sauer and Meyer, 1992), and error introduced by estimating average velocity from maximum velocity (Chen and Chiu, 2002).

2.5 Calculation of tidal prism from tidal stage and geomorphic data

Field measurements of water volume for spring tidal cycles were compared with values of spring tidal prism calculated for each marsh:

$$V_p = T_r A_{ws} \quad (2)$$

where V_p is spring tidal prism (m^3), T_r is spring tidal range (m), and A_{ws} is waterway surface area (m^2). Waterway surface area was determined from air photos. Local tidal range (and tidal period) for each individual marsh system is controlled by tidal stage and the elevation of the inlet channel relative to the marsh platform. For the smaller channels, inlet depth limits tidal stage and inundation time. Maximum channel depth for each inlet was determined from the inlet width (W) to inlet area (A_c) relationship, and assuming triangular geometry that was indicated by field measurements. The relationship of spring tidal prism to geomorphic parameters (inlet cross sectional area and marsh surface area) was also examined and compared to field measurements of spring tide water volume.

2.6 Field mass balance measurements of nitrate retention over spring tidal cycles

Water sampling for N species (NH_4-N, NO_2-N, NO_3-N) was conducted over spring tidal cycles. This maximum flooding condition was chosen to provide comparisons with laboratory conditions of marsh surface flooding, which produce maximum nitrate retention rates (Reddy et al., 1984). Water samples for the outgoing tidal cycle were measured in concert with gauge height and velocity measurements. Samples taken during flooding tides indicate that concentrations of N species remain nearly constant on the rising stage (Fig. 2a); therefore, sampling schemes were adopted that included only a portion of the flooding tide to obtain average incoming concentrations, along with the entire falling tide at each channel inlet sampling (Fig. 2b–d). Water samples were taken at 30 min intervals and filtered in the field with 45 µm syringe filters. The samples were immediately frozen and analyzed within several weeks for dissolved inorganic nitrogen series (NH_4-N, NO_2-N, NO_3-N) using standard photometric methods and ion chromatography (Solorzano, 1969; Keefe et al., 2004). Analytical error of ±2 µmol, determined by the mechanical specifications of the equipment, was considered in all nitrate retention calculations.

Nitrate was the only form of nitrogen that shows significant variation over the tidal cycle, and is therefore the focus of this study (Fig. 2b–d). Nitrate retention was determined by subtracting the outgoing flux of nitrate from the average incoming nitrate flux for each tidal marsh for each time increment:

$$\mathrm{NR} = \sum [Q_t(N_{\mathrm{i}(t)} - N_{\mathrm{o}(t)})] \tag{3}$$

where NR is nitrate retention (mol); Q_t is discharge ($\mathrm{l\,s^{-1}}$); $N_{\mathrm{i}(t)}$ is initial [NO_3-N] of tidally introduced water (µmol), and $N_{\mathrm{o}(t)}$ is [NO_3-N] of outgoing tidal water at time t in µmol. One of the advantages of using mass balance calculations of nitrate retention is that it provides measurements of nitrate retention for individual marshes for a given tidal cycle, time of year, and initial nitrate concentration. No assumption is made of nitrogen retention processes within each individual marsh, although previous work suggests that marsh surfaces are primary sites for nitrate retention (Seldomridge, 2009).

Nitrate retention data were compared with both measured water volumes over a tidal cycle and marsh area to determine whether nitrate retention could be expressed as simple functions of either parameter. These results then guided the development of relationships between nitrate retention and geomorphic parameters.

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3 Results

3.1 Cumulative geomorphic distributions

The data in the cumulative distributions can be described as inverse power law functions (Fig. 3). The power law for the cumulative number of marsh surface area is:

$$N = 4712.3A^{-0.54}, \quad n = 142, \quad R^2 = 0.97 \tag{4}$$

where N is the cumulative number of marshes with area $> A$. The power law for the cumulative number of channel lengths is:

$$N = 2224.1L^{-0.78}, \quad n = 242, \quad R^2 = 0.90 \tag{5}$$

where N is the cumulative number of channels with lengths $> L$. Finally, the power law for the cumulative number of inlet widths is:

$$N = 133.2W^{-0.59}, \quad n = 267, \quad R^2 = 0.92 \tag{6}$$

where N is the cumulative number of inlets with a width $> W$. The smallest marsh inlet width measured from air photo data is 0.2 ± 0.05 m; this lower boundary was validated by field measurements.

3.2 Relationships between geomorphic variables

Inlet width measurements from air photos were the most accurate of the 3 geomorphic parameters (within 1 % of measured values). Visibility of small inlets on photographs provided an almost complete inventory of inlet channels; therefore, the number of marsh inlets was used to define missing data for the other geomorphic parameters. Comparison of the number of inlet widths measured with channel length and marsh area measurements indicated that 47 % of the total number of marsh area measurements (for the smallest marshes) and 9 % of the channel length data are missing from

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the measured populations although the width of the associated marsh inlet was identified. Relationships among the geomorphic variables were examined and are shown in Fig. 4; several of these relationships are given below:

$$L = 1.3A^{0.53}, \quad n = 142, \quad R^2 = 0.79 \tag{7}$$

$$W = 0.2A^{0.65}, \quad n = 142, \quad R^2 = 0.47 \tag{8}$$

Where L is the channel length, W is the inlet width, and A is the marsh surface area. Missing values for marsh surface area and channel length were estimated from their relationship to marsh width (e.g., Eq. 8).

Stream order was evaluated for each individual marsh channel network; maximum stream order for each marsh was determined, and the relationship between stream order and marsh area is shown in Fig. 4c. Stream order depends upon the choice of ordering system, the resolution of aerial photos and maps, and often fails to discern characteristics between network structures (Kirchner, 1993; Rinaldo and Rodriguez-Iturbe, 1998); therefore, it was not used to model ecosystem nitrate retention in this study.

3.3 Relationship of spring tidal volume to geomorphic parameters

The relationships between spring tidal prism (V_p) and both marsh surface area (A), and inlet channel cross sectional area (A_c) are shown in Fig. 5. The relationship between bankfull inlet cross sectional area and inlet width was developed from data on 18 channel inlets (Table 1; Fig. 5a):

$$A_c = 0.20W^{1.4}, \quad n = 18, \quad R^2 = 0.88 \tag{9}$$

This relationship was used to estimate average and maximum inlet depth for each channel, which can be expressed as elevation relative to mean lower low water (Fig. 5b). The relationship of calculated spring tidal prism to inlet channel cross sectional area (Fig. 5c) is:

$$V_p = 0.004A_c^{1.02}, \quad n = 142, \quad R^2 = 0.65 \tag{10}$$

The field measurements of hydrologic volume over a tidal cycle are indicated in Fig. 5c as the three solid squares that plot near the central tendency of this relationship.

The calculated tidal prism was expressed as a power function of each of the 3 geomorphic parameters (marsh area, channel length, and inlet channel width; Fig. 6). Field measurements of tidal water volumes (tidal prism) for the same tidal stage are also indicated on these diagrams. These relationships indicate significant scatter between each geomorphic variable and tidal prism. In addition, there are systematic differences between the tidal prism estimates of water volume and the field measurements for all 3 geomorphic parameters (Fig. 6). These systematic differences suggest that the tidal prism method under-estimates the amount of water carried into small tidal systems, but over-estimates the amount carried into large tidal systems.

3.4 Mass balance results of nitrate retention

The autumn data mass balance measurements of nitrate retention for each of the three marshes is shown in Table 1. These data indicate that the ratio of nitrate retention to water volume is constant for a given set of conditions. The data (Fig. 7) indicate a nearly linear relationship between water volume and nitrate retention for spring (high) tides, which aligns with the multi-year data for the entire growing season:

$$\mathrm{NR} = 0.0045V^{1.1}, \quad n = 6, \quad R^2 = 1.0 \tag{11}$$

Where NR is nitrate retention (mol) and V is the tidal volume water fluxed through the inlet channel mouth (m^3). When the exponent of 1.1 is rounded to 1, the trend is linear and can be simplified to:

$$\mathrm{NR} = aV_{\mathrm{in}} - bV_{\mathrm{out}} = cV \tag{12}$$

Where NR is nitrate retention (mol), a is the integrated average nitrate concentration (mol) on the incoming tide, b is the integrated average nitrate concentration (mol) on the outgoing tide, V is the volume of water flux (l), and c is the concentration of retained

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nitrate (mol). If $V_{in} = V_{out}$, which is the case for tides with minimal water storage or evapotranspirative losses, the equation is simplified to:

$$NR = (a - b)V = cV \quad (13)$$

The relatively constant incoming nitrate concentrations were used to evaluate total nitrate flux into the tidal marshes (Table 1). These data indicate that approximately 30 % of the total nitrate flux into the marshes was retained for the measured spring tides (Table 1). The constant ratio of NR/V (Table 1; Fig. 7) for varying values of incoming nitrate concentration suggest that retention is not limited by the range (23 to 57 ± 2 µmol) of initial, incoming concentrations measured for this study.

3.5 Comparison of ecosystem calculations of nitrate retention and evaluation of geomorphic parameters

The relationship between water volume and nitrate retention relationship (Fig. 7) and the field-based relationship between water volume and each geomorphic parameter (Fig. 6) were combined to determine an equation between each geomorphic variable and nitrate retention (Table 2). These equations were then applied to the entire population of each geomorphic variable (Fig. 3) to estimate total nitrate retention for this TFW ecosystem (Fig. 8). Estimated total nitrate retention for the geomorphic parameters varied considerably; the estimate based on marsh area was only 44 % of the value estimated from inlet width data. Nitrate retention for the reference spring tides (autumn 2008 and 2011) was 1738.9 ± 44.6 mol NO_3-N based on marsh area data, 2790.1 ± 31.2 mol NO_3-N based on channel length data, and 3961.2 ± 135.8 mol NO_3-N based on inlet width data. When the channel length and marsh surface area data were adjusted to account for missing measurements, the total nitrate retention is closer to the estimate based on inlet width (Fig. 8). The total nitrate retention based on adjusted marsh surface areas is 2254.9 ± 44.6 mol NO_3-N, and for adjusted channel length is 2892.9 ± 31.2 mol NO_3-N.

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The distribution of total nitrate retention among the individual marshes as a function of channel width and marsh surface area is shown in Fig. 8B-C. As a function of channel width, the 8 widest channels (3 % of total; ranging from 43.86 m wide to 93.39 m wide) are responsible for 50 % of the NR. As a function of marsh surface area, the 11 biggest marshes (4 % of total marsh area) are responsible for 50 % of the NR; in sum these marshes cover 3 227 913 m^2 or approximately 80 % of the TFW ecosystem. Therefore, these largest marshes (top 4 %) represent a larger proportion of the total marsh area (80 %) than of total nitrate retention (50 %).

4 Discussion

4.1 Geomorphic data and geomorphic relationships

In this study, the inlet width data were accurately measured from imagery data, relatively easy to field verify, and provided a nearly complete data base that could be used to evaluate the quality of the other geomorphic data bases. All of the geomorphic parameters exhibited power law behavior of cumulative data. Distributions were confined to 3 orders of magnitude for inlet width (Fig. 3), which suggest that minimum channel size may be affected by external controls, such as vegetation growth (Hickin, 1987; Rinaldo et al., 1999b; Montgomery, 1999). The upper limit of inlet size defines the maximum size of a tidal marsh that can be sustained in this system (Jenner, 2011), which is likely controlled by tidal stage and available space along the river width.

Although total length of the main channel network provides a measure of the conduit that conveys nutrient-rich waters into marsh interiors (Myrick and Leopold, 1963; Fagherazzi et al., 1999; Rinaldo et al., 1999a), this geomorphic parameter was also difficult to measure, particularly for large, complex marshes. In this study, the geomorphic system was composed of individual marshes arrayed along the length of the tidal Patuxent River, which is not directly analogous to the geomorphic organization of a large tidal system (e.g., Rinaldo et al., 2004). In this study, we found that total channel length was more closely related to tidal prism than marsh watershed area, which is the opposite of the result obtained by Marani et al. (2003) for a large complex tidal marsh.

Previous studies have identified marsh surfaces as important sites for biogeochemical cycling (e.g., Bowden et al., 1986), and marsh area has previously been used as a scaling parameter to extend laboratory measurements of denitrification rates to field settings. Previous studies indicate that microtopography can greatly increase the overall area available for NR (Wolf et al., 2011); this study suggests that microtopography is only one of the difficulties presented in using marsh surface area as a scaling parameter. Non-synchronous flooding of surfaces of similar elevations as a function of travel time from the tidal inlet is an important issue in this system.

In this study, each freshwater tidal marsh was connected by a well-defined inlet channel to the main Patuxent River estuary. Thus, the inlet channel cross section area and tidal hydrodynamics control the amount of water, sediment, and solutes that move into the marshes (Fagherazzi et al., 1999). Using channel width as the geomorphic unit for scaling provided the *highest* estimate of ecosystem nitrate retention (Fig. 8) because every inlet channel and thus every marsh system was included in the ecosystem evaluation. This geomorphic parameter is also easily adaptable to other tidal conditions through the relationships between channel width and hydraulic parameters (depth, velocity, area, discharge; Myrick and Leopold, 1963; Marani et al., 2003). Measurements of vegetative flow resistance can provide information to predict water fluxes with seasonally varying hydraulic conditions. Thus, for this tidal freshwater wetland ecosystem, with the simple arrangement of the marsh inlets along the sides of the estuary, inlet width provides the most complete and accurate data for estimating tidal water volumes and nitrate retention.

4.2 Hydrologic controls on nitrate retention

Tidal marshes are self-organized systems in which the marsh area coevolves with hydrologic flux to form the channel network system (Bak et al., 1988; Odum, 1988). This self-organization of tidal marsh networks generates systematic relationships between geomorphic characteristics and hydraulic characteristics (Fig. 4a,b). Mass balance studies indicated a nearly linear relationship between water volume and nitrate retention for spring (high) tides (Eq. 11), which suggests that nitrate retention is limited by hydrologic flux in this system (Seldomridge and Prestegaard, 2011). This relationship between hydrologic flux and nitrate retention relationships was similar for different seasons and tidal stages (Fig. 7). These data suggest that although marsh surface area may be the dominant site for nitrate retention (Seitzinger, 1988; Cornwell et al., 1999), the ability of water to move through the system, even for the highest tides with minimum channel flow resistance, is the greatest control on nitrogen processing. Marsh areas that are available for processing have limited activity due to limitations in water reaching these sites. Nitrate retention includes a variety of processes such as denitrification, biotic assimilation, burial, and/or recycling. These processes are seasonally variable and may be controlled by factors such as temperature, the availability of organic matter, amount of oxygen, nitrogen availability, and composition of the microbial community (e.g., Seitzinger, 1988, 1994; Cornwell et al., 1999; Wallenstein et al., 2006). Although these controls may be seasonally important, results from this study suggest that nitrate retention in these freshwater tidal wetlands is a relatively simple function of water volumes. Evaluation of additional hydrodynamic data is needed to use geomorphic data (inlet width, inlet area) to predict tidal volumes, and thus nitrate retention for other tidal stages and seasons.

4.3 Spatial distribution of nitrate retention

Although the small-sized marshes systems are the most common (Fig. 3), the spatial distributions of nitrate retention indicate that a small number of the biggest marshes are responsible for the majority of retention (Fig. 8b,c). The largest 4 % of the marshes by area represented 80 % of the total area and retained 50 % of the total nitrate. Although numerous, the small marshes contributed small proportions to the total nitrate retention due to the short inundation times of these high elevation surfaces. Previous studies suggest that small marshes with high surface area to volume ratios are the important sites for nitrate retention (e.g., Simpson et al., 1983; Groffman, 1994; Boynton et al., 2008). Although we also observed the largest surface area to volume ratios for the small systems (Table 1), it is the volume of water that limits the nitrate retention in this system, not the area to volume ratio.

5 Conclusions

The appropriate geomorphic unit for scaling an ecosystem function must be chosen based on both underlying controls (e.g. water volume), and also on data availability and accuracy of measurement. For this study, field measurements of in situ nitrogen processing rates on multiple scales were necessary to determine the appropriate scaling parameters to estimate ecosystem nitrate retention. We suggest that mass balance measurements might be appropriate as fundamental steps to determine scaling parameters in other systems. Although the results of this study appear to be related to the geomorphic organization of TFW along the main estuary, and thus might not be directly applicable to other tidal freshwater wetlands, the integrated mass balance, geomorphic approach should be applicable to other ecosystems. In addition, any other ecosystem function that is linked to hydrologic flux, such as sediment transport and deposition, allochthonous organic carbon retention, and perhaps sulfate retention, can be analyzed using this approach. This study presents spatially-distributed estimates of nitrate retention for one representative high tidal stage. Additional work is necessary to determine hydrodynamic and other data required to evaluate nitrate retention for temporally-varying conditions (e.g. seasonal and tidal variations in hydrodynamic and nitrogen processing).

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Table 1. Geomorphic characteristics of marshes and mass balance measurements for Fall 2008.

	Site 1	Site 2	Site 3
Marsh surface area (m^2)	670.6	5705	536873.4
Total channel length (m)	21.6	124.6	1577.3
Inlet channel width (m)	4.15	6.5	41.7
Stream order	2	3	7
Inlet (maximum) depth (m)	0.59	0.79	2.0
Inlet channel area (m^2)	1.26	2.5	41.1
Water volume (m^3)	353 ± 14	1218 ± 61	16524 ± 826
Nitrate retained (mol)	3.4 ± 0.3	10.6 ± 0.2	144.2 ± 6
Nitrate retention rate per area ($mol\,m^{-2}$)	4439	1822	326
Nitrate retention rate per volume ($mol\,l^{-1}$)	8.5 ± 0.6	8.7 ± 0.02	8.7 ± 0.1
Incoming nitrate (mol)	9	32	430

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Table 2. List of equations describing geomorphic, hydrologic, and biogeochemical relationships.

Geomorphic-hydrologic	
$V = 7.81A^{0.58}$	$n = 3$, $R^2 = 1$
$V = 18.15L^{0.91}$	$n = 3$, $R^2 = 0.99$
$V = 44.63W^{1.6}$	$n = 3$, $R^2 = 0.98$
Geomorphic-biogeochemical	
$NR = 0.0045V^{1.1}$	$n = 13$, $R^2 = 0.98$
$NR = 0.038A^{0.61}$	$n = 6$, $R^2 = 0.96$
$NR = 0.09L^{0.97}$	$n = 6$, $R^2 = 0.96$
$NR = 0.25W^{1.7}$	$n = 6$, $R^2 = 0.92$

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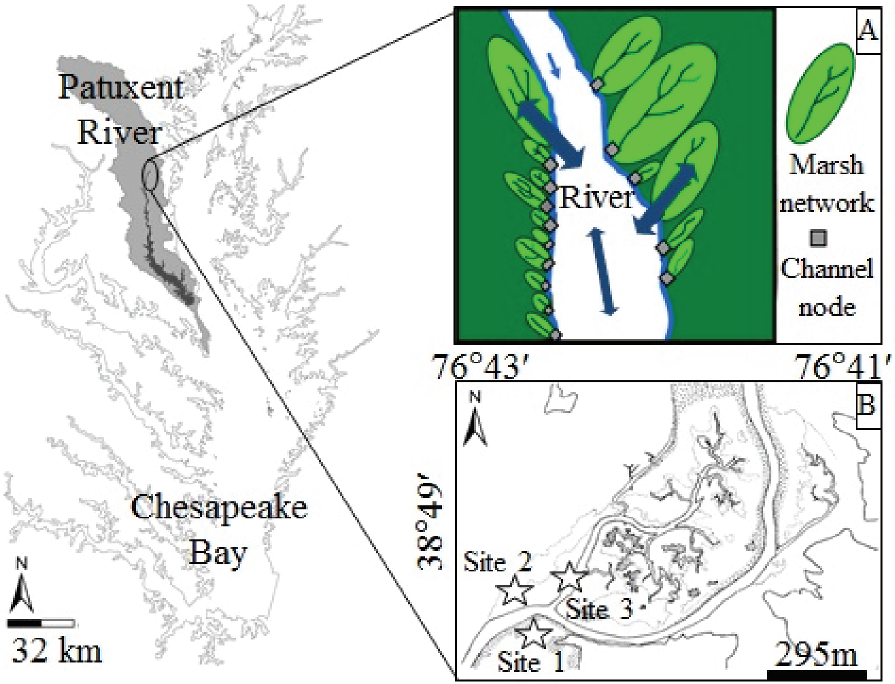

Fig. 1. Study area located in the tidal freshwater portion of the Upper Patuxent River, Maryland. **(A)** Schematic diagram showing the organization of tidal marshes along the river. Tidal fluxes are controlled by inlet channel geomorphology (governing node). **(B)** Map of selected marshes for mass balance measurements. Marsh areas (m^2) are: Site 1: 670.6, Site 2: 5705, Site 3: 536 873.4.

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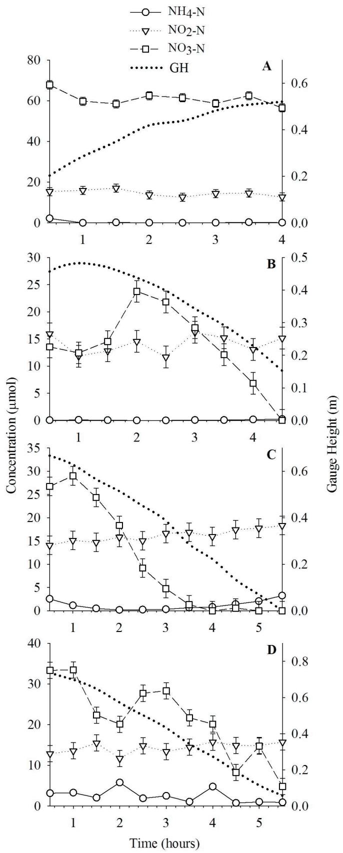

Fig. 2. Examples of water chemistry measurements. **(A)** Constant concentrations on incoming tides at Site 1 on 24 September 2008. **(B)** Nitrogen concentrations and tidal stage for the ebbing tidal cycle at Site 1 on 20 September 2008. The nitrate concentrations decrease with the dropping tidal stage. **(C)** Data for the ebbing tide at Site 2 on 1 October 2008. **(D)** Data for the ebbing tide at Site 3 on 1 October 2008.

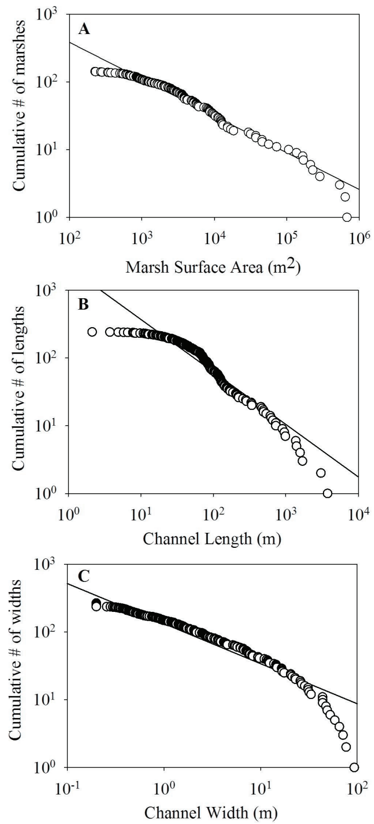

Fig. 3. Geomorphic data for the tidal freshwater portion of the Patuxent River. (A**)** Cumulative number of marsh areas less than or equal to indicated value ($N = 4712.3A^{-0.54}$, $n = 142$, $R^2 = 0.96$). **(B)** Cumulative number of channel lengths less than or equal to indicated size ($N = 2224.1L^{-0.78}$, $n = 242$, $R^2 = 0.90$). **(C)** Cumulative number of inlet channel widths less than or equal to indicated value ($N = 133.23W^{-0.59}$, $n = 267$, $R^2 = 0.92$). Standard error is less than size of data points.

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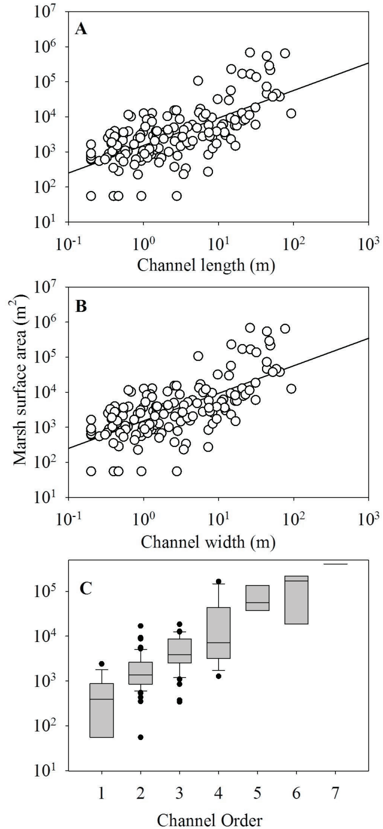

Fig. 4. Geomorphic relationships of channel order, inlet width, and total channel length to marsh surface area of tidal freshwater marshes along the Patuxent River Estuary. **(A)** $L = 1.3A^{0.53}$ ($n = 142$, $R^2 = 0.79$). **(B)** $W = 0.2A^{0.65}$ ($n = 142$, $R^2 = 0.47$). Standard error is less than the size of each data point. **(C)** Box plot of marsh surface areas for each stream order.

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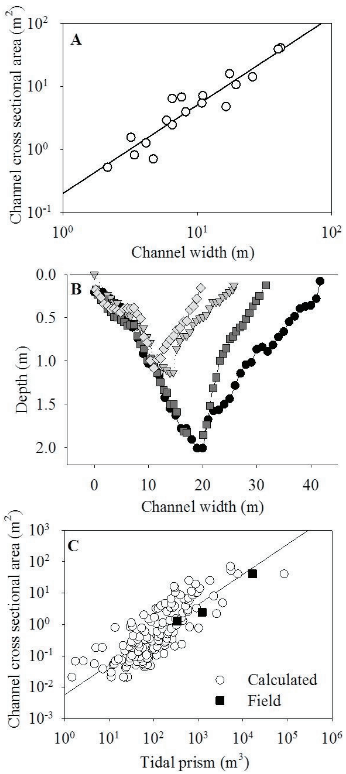

Fig. 5. Calculated spring tidal prism for tidal freshwater wetlands. **(A)** Relationship between inlet width and cross sectional area. **(B)** Inlet channel cross sectional areas plotted relative to the elevation of the marsh platform. Inlets with widths > 16 m experience the entire spring tidal range, whereas tidal range in the smaller inlets is constrained by inlet elevation, so that they experience a portion of high tidal stages. **(C)** Relationship between inlet cross sectional area and tidal prism (Eq. 10). Squares indicate field measurement of spring tide water volumes for the 3 sampling sites.

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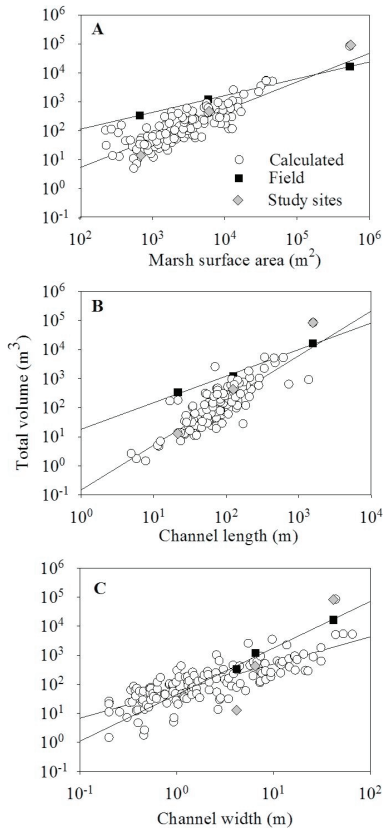

Fig. 6. Relationship of calculated tidal prism to: **(A)** marsh surface area, **(B)** channel length, and **(C)** inlet channel width. Field measurements are shown as black squares, gray triangles highlight predicted tidal prism for the corresponding study sites.

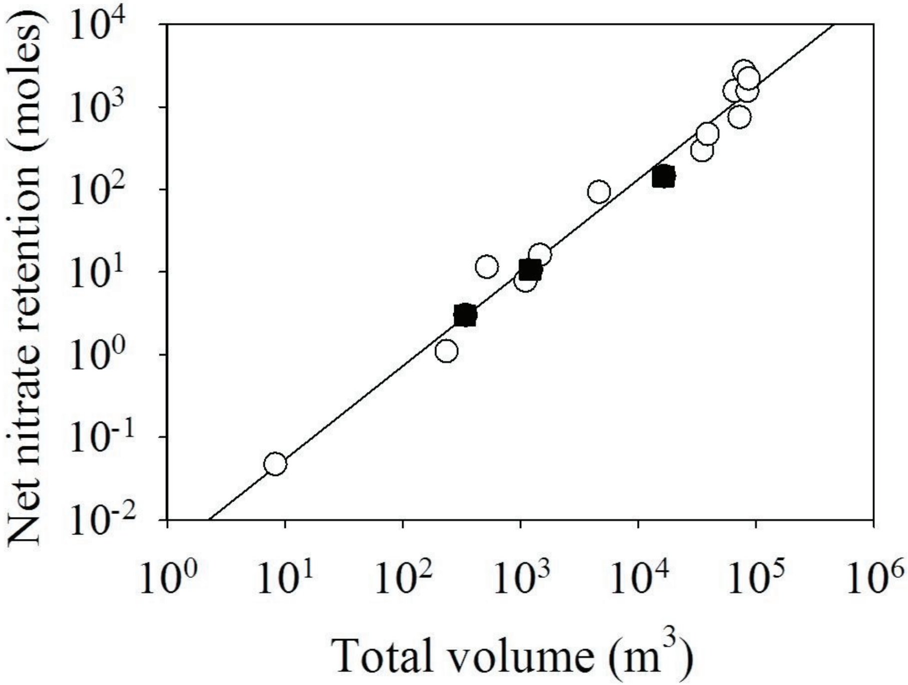

Fig. 7. Relationship between net nitrate retention over a tidal cycle and water volume. Data are reported for the 3 sampling sites for various tides in 2008, 2010, and 2011. Nitrate retention is a simple function of hydrologic flux that varies over 5 orders of magnitude. Data for spring (high tides) in autumn 2008 and 2011 follow the relationship: $NR = 0.0045V^{1.1}$ ($n = 6$, $R^2 = 1.0$).

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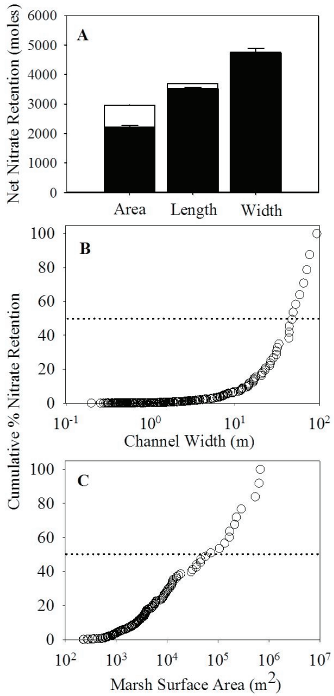

Fig. 8. Total ecosystem nitrate retention calculated from each of the 3 geomorphic variables. **(A)** Nitrate retention estimated from marsh surface area data is 1738.9 ± 44.6 mol NO_3-N, from channel length is 2790.1 ± 31.2 mol NO_3-N, and from channel width is 3961.16 ± 135.8 mol NO_3-N. Stacked white bars indicate additional retention calculated by adding in the missing geomorphic data, which were predicted from geomorphic relationships to inlet width. **(B)** Spatial distribution of nitrate retention as a function of channel width; the 8 largest channels are responsible for 50 % of total retention. **(C)** Spatial distribution of nitrate retention as a function of marsh surface area; the 11 largest marshes are responsible for 50 % of total retention.

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