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Nutrient Retention and Release in Eroding Chesapeake Bay Tidal Wetlands

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Research Impact Statement: Tidal marsh erosion results in the diminishment of nutrient ecosystem services from both the loss of ongoing nutrient sequestration and the export of reactive nutrients to tidal waters.

ABSTRACT: The worldwide loss of coastal wetlands has traditionally been addressed as the loss of ongoing nutrient retention ecosystem services. However, nutrient remineralization from eroded particles may further exacerbate water quality degradation. Using data on nutrient burial and denitrification from northern Chesapeake Bay, along with estimates of the bioavailability of eroded marsh particulates, the changing role of wetlands as an important sink for nutrients is examined. Although the erosion of wetlands results in the reintroduction of nitrogen and phosphorus into open-water habitats, the potential for exacerbating eutrophication is highly diminished by the low lability of wetland organic matter. The impact of such erosion on the cycling of Fe-bound phosphorus from marsh soils is highly dependent on both the amount of inorganic P, its solid phase association with Fe, and its potential remobilization from the estuarine sediments into which it is deposited. Although nutrient sequestration in newly constructed wetlands built from dredged materials suggested a rapid development of nutrient sequestration, a better understanding of nutrient ecosystem services provided by marshes created by transgression into uplands is necessary for understanding the long-term nutrient retention value of coastal wetlands.

(KEYWORDS: estuaries; restoration; eutrophication; biogeochemistry; nutrients; wetland loss; denitrification.)

INTRODUCTION

Tidal wetlands are important sinks for nitrogen and phosphorus in the Chesapeake Bay and other coastal ecosystems (Merrill and Cornwell 2000; Loomis and Craft 2010), with N and P burial and denitrification providing valuable ecosystem services (Jordan et al. 2011; Sousa et al. 2012). These biological and physical removal processes have been observed in the tidal fresh-water part of several different Chesapeake Bay subestuaries (Boynton et al. 2008; Hopfensperger et al. 2009). The burial of N and P also represents a large sink of these elements in fresh to saline coastal wetlands (Craft and Richardson 1993), including the Chesapeake Bay (Malone et al. 2003; Palinkas and Cornwell 2012). The general presumption is that C, N, and P buried below the root zone is "permanently" buried, though inorganic P bound to iron oxides may be remobilized under sulfate-reducing conditions (Roden and Edmonds 1997). Nitrogen is generally buried as organic N, while P can be buried in both organic and inorganic forms. In addition to nitrogen burial, there has been considerable interest in the connection of marshes with estuarine waters: the outwelling of organic materials may be an important source of nutrition and nutrients to receiving waters (Heinle and Flemer 1976; Nixon 1980; Childers et al. 2000).

Wetland loss results in the diminishment of these nutrient sinks as these intertidal vegetated areas are converted to open water environments. In the Gulf of

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Mexico, eroded wetland organic material contributions to anoxia in the Gulf of Mexico “dead zone” (Bianchi et al. 2011) are inconsistent with mass balance and modeling studies which suggest that Mississippi River nitrate results in the production of algal organic matter leading to hypoxia (Das et al. 2011). The microtidal physical regime of Chesapeake Bay marshes (Kearney and Turner 2016) increases the susceptibility of wetland losses associated with sea-level rise (Kearney et al. 2002; Kirwan and Megonigal 2013), with transgression mitigating part of these losses (Schieder et al. 2018). In the Chesapeake Bay, both direct consumption of oxygen by decomposing wetland organic matter and the release of N and P from eroding wetland soils may impact nutrient and oxygen balances. Due to water quality impairments in the Chesapeake Bay (Kemp et al. 2005), considerable efforts have been made over a number of decades to control inputs of nitrogen and phosphorus (Harding et al. 2019). However, marsh creation via restoration and transgression into uplands has the potential to partially offset the loss of nutrient removal ecosystem services resulting from marsh erosion.

Two aspects of nutrient balances associated with wetland loss are considered here. First, the loss of nutrient removal ecosystem services associated with wetlands is estimated, using literature data on denitrification and the burial of N and P (Figure 1a). Second, the results of a marsh soil decomposition study are used to examine the potential for nutrient release and oxygen uptake from eroded wetland soil (Figure 1b). Here, for a given area of wetland, we estimate the rates of nutrient retention and denitrification against the potential releases of N and P via erosion, including consideration of the portion of the N and P that may become bioavailable after erosion. We present the rates of N retention at Poplar Island marshes constructed using dredged materials (Cornwell et al. 2020; Staver et al. 2020) to examine if such marsh creation opportunities create equivalent nutrient removal. Because of the range of potential inventories of marsh N and P, nutrient burial rates, and possible rates of wetland erosion, the broader utility of this analysis is the identification of a calculation framework for changes in nutrient ecosystem services in eroding wetlands.

METHODS

The estimation of nitrogen and phosphorus retention in Chesapeake Bay wetlands utilizes data collected over three decades and from many different northern Chesapeake Bay wetland sites using consistent methods. Data from three different types of studies were used in this analysis, including net burial rates of N and P estimated from ^{210}Pb-based geochronology, measurement of denitrification using changes in N_2:Ar ratios in the overlying water of intact cores, and long-term decomposition measurements using slurried sediment from multiple locations.

Study Sites

Data from 10 wetland areas were used in this study, with nutrient burial data from five wetland areas, denitrification from six wetland areas, and

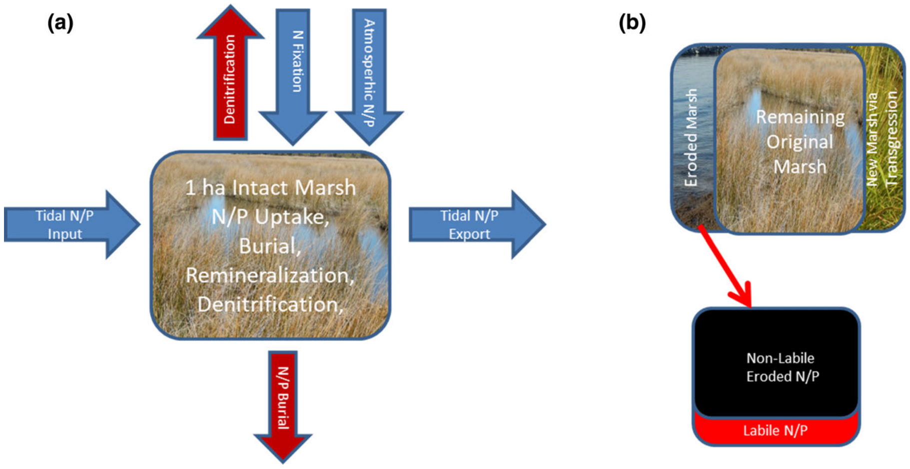

FIGURE 1. Idealized nitrogen balance of a tidal wetland. (a) The net retention of N and P via burial, plus the loss of N via denitrification represent the nutrient removal ecosystem services of the wetland. (b) Wetland loss, or transgression, with a loss of N and P via erosion. The erosive loss of N and P has a labile component which can release reactive N or P to the estuary. The net nutrient ecosystem service of this wetland is nutrient removal within the intact or transgressed wetland minus the release of reactive N and P.

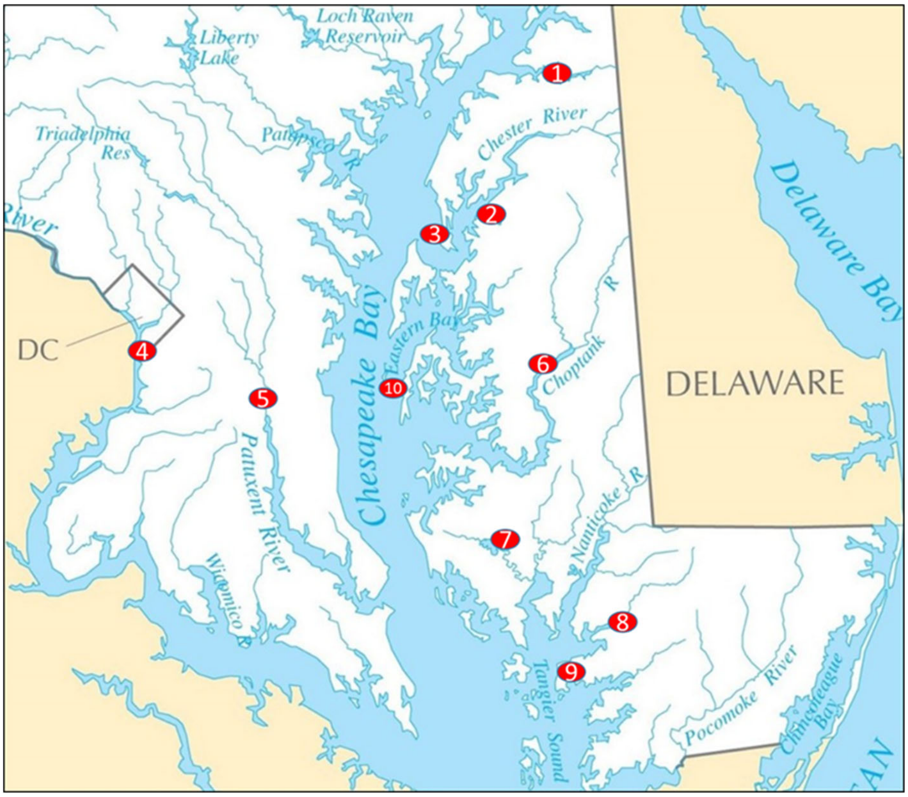

FIGURE 2. Locations in the upper Chesapeake Bay where wetlands were sampled for denitrification and/or burial of N and P. The numbers correspond to the information in Table 1.

decomposition measurements from four wetland areas (Figure 2; Table 1). All collections were from low marsh habitat, with the marsh plant communities largely set by salinity (Baldwin et al. 2012). The nutrient burial data are most abundant in three areas (9–25 cores from each), with the Patuxent River estuarine gradient receiving nutrient inputs from point sources (Boynton et al. 2008), and both Choptank River and Monie Bay watersheds heavily influenced by agriculture (Fisher et al. 2006). Denitrification data were taken from studies in a number of tidal subestuaries, including the heavily nutrient-impacted Sassafras River (Ana I. Sousa, unpublished data), agriculturally dominated Corsica River (Jeffrey C. Cornwell, unpublished data), Dyke Marsh on the nutrient-enriched upper Potomac River (Hopfensperger et al. 2009), the urban and agriculturally impacted upper Patuxent River (Boynton et al. 2008), and at Poplar Island, a constructed wetland area built using nutrient rich fine-grained dredged materials from the upper Chesapeake Bay navigation channels (Cornwell et al. 2020; Staver et al. 2020). Although the denitrification data used here are mostly from published papers, available reports, and a dissertation, the unpublished data from Sousa and Cornwell use identical measurement techniques as the published work, with the approach described in Methods.

Nitrogen and Phosphorus Burial

The data for N and P burial have been collated from reports and publications and have used the same technical approach. Sediments for ^{210}Pb-based nutrient burial were collected with a Russian peat corer and generally sectioned into 2.5 cm near the surface and either 5 or 10 cm sections at greater depths. Samples were stored in a vial, kept cool until determination of bulk density via water displacement, and dried at 65°C. Samples were homogenized with a mortar and pestle and analyzed for ^{210}Pb via alpha counting of the daughter nuclide ^{210}Po after HNO_3/HCl extraction (Owens and Cornwell 1995). The accretion rate was calculated using the constant initial concentration calculation approach (Robbins 1978). Additional analyses conducted on each section included carbon and nitrogen using a CHN analyzer (Cornwell et al. 1996), and total phosphorus using HCl extraction of ashed sediment (Aspila et al. 1976).

Denitrification

Denitrification rates (Table 1) were estimated using intact cores of either 7 or 10 cm inner diameter, followed by incubation in a temperature-

TABLE 1. Sites used for measurement of denitrification, nutrient burial, and decomposition in tidal marshes. Mean rates are shown for N burial, P burial, and denitrification. The N burial rate at Poplar Island is estimated using C burial rates and a molar C:N of 19.1. Mean decomposition rate (±S.D.) units are inverse day and are determined from oxygen uptake, assuming equivalence to CO_2 production rates, and dividing rates by the carbon concentration.

Map key	Site	Salinity	N burial g N/m^2/year	P burial g P/m^2/year	DNF g N/m^2/year	Decomp day^{-1} $(\times 10^{-5})$	References
1	Sassafras River	Fresh			15.1		Ana I. Sousa, unpublished
2	Corsica River	Fresh	14.3	1.4	32.4		Jeffrey C. Cornwell, unpublished; Palinkas and Cornwell (2012)
3	Eastern Neck NWR	Mesohaline				5.8 ± 1.7	This study
4	Dyke Marsh	Fresh			18.0		Hopfensperger et al. (2009)
5	Upper Patuxent/Jug Bay NERRS	Fresh-Oligohaline	18.3	3.76	14.7	9.1 ± 8.2	Merrill (1999); Boynton et al. (2008)
6	Choptank River	Fresh-Oligohaline	21.2	1.72			Malone et al. (2003)
7	Blackwater NWR	Oligohaline	—	—	—	6.1 ± 2.5	This study
8	Monie Bay NERRS	Oligohaline-Mesohaline	10.6	0.63	Bank 16.7 Mid 0.0		Merrill (1999)
9	Deal Island	Mesohaline	—	—		5.7 ± 3.0	This study
10	Poplar Island — Wetland Restoration	Mesohaline	12.6	—	16.2		This study; Staver et al. (2020)

Notes: DNF, denitrification; NERRS, National Estuarine Research Reserve; NWR, National Wildlife Reserve.

controlled chamber (Owens and Cornwell 2016). Changes in the N_2:Ar ratio were determined by mass spectrometry (Kana et al. 1994) and increases in N_2 were determined by regression of N_2 concentrations. This technique required flooded cores and as in other studies (Elsey-Quirk et al. 2013) we assume that rates during flooded conditions are the same as when there is no overlying water. The denitrification rates presented here are net fluxes of N_2 and may underestimate N_2 fluxes because of N fixation, or overestimate the rates of canonical denitrification if anammox is an important N_2-producing process (Burgin and Hamilton 2007).

Decomposition Experiments

For sediment decomposition rate studies, single cores were collected from three low marsh sites at the Blackwater National Wildlife Reserve (BNWR), a wetland complex experiencing losses of marsh area to pond and lake formation (Schepers et al. 2017). Sites were chosen from areas in which marsh loss was evident. A Russian peat corer was used to collect cores with minimal compression. The export of sediment from BNWR oligohaline/brackish wetlands occurs through the Blackwater River into the adjacent mesohaline Fishing Bay, a shallow water system without hypoxia/anoxia (Stevenson et al. 1985). Two cores were collected from the Eastern Neck Wildlife Refuge (ENWR), a 9.25 km^2 island with eroding brackish marshes at the mouth of the Chester River subestuary. The two sites were from a fringing wetland area characterized by wetland loss, with one core site showing exposed peat layers without intact marsh above it. Eroded materials from this site likely deposit into deep anoxic channels in the Chesapeake Bay. A single core was collected from Jug Bay, a tidal fresh-water National Oceanic and Atmospheric Administration National Estuarine Research Reserve Site in the upper Patuxent River (Seldomridge and Prestegaard 2014); a gas-filled void was noted from 17 to 43 cm. This site is near an abandoned rail bed that has been previously characterized for wetland accretion and nutrient burial (Khan and Brush 1994). A single core was collected from a brackish *Spartina alterniflora* marsh site in Deal Island, Maryland, a deteriorating wetland with ponding (Qi et al. 2021).

Using changes in the cores to visually determine core segmentation, in most cases, sediments were sectioned into three samples, accommodating the mass of sediment needed for both solid phase characterization and estimates of decomposition. From these sections, 20 mL of homogenized sediment was dried at 65°C in weighed pans to determine bulk density and moisture content, with C, N, and P analyzed as in the accretion data. In addition, inorganic P was measured using HCl extraction without ashing (Aspila et al. 1976). Chromium-reducible sulfur (CRS), an estimate of dissolved and particulate reduced sulfur often dominated by pyrite sulfur, was analyzed after distillation of H_2S, trapping in sulfide antioxidant buffer, and titration with lead persulfate (Cornwell and Morse 1987).

Each sediment horizon used for chemical characterization and decomposition were manually homogenized without addition or deletion of water. For the decomposition experiments, 20 mL of homogenized sediment was added to a 250-mL wide mouth septa jar, 150 mL of water (salinity of 5 or 15) was added, and all incubations started under the aerobic conditions likely to occur during marsh erosion/transport. After the septa caps were attached, jars were placed on a shaker table with ~30 oscillation/min under dark conditions at 20°C. We used sea water diluted to a salinity of 5 for the Blackwater and Jug Bay sites, simulating their erosion into downstream oligohaline conditions. At Eastern Neck and Deal Island, the local brackish conditions made a salinity of 15 relevant.

At each sample time point, the pH was measured using a flat combination electrode calibrated with NIST buffers; a small sample (2 mL) was removed by a syringe for the analysis. The measurement of oxygen was carried out with a flow through cell using a fiber-optic oxygen meter. A sample was pulled into the small flow cell using a syringe and the sample was subsequently returned to the jar. The number of time oxygen points ranged from 12 to 16 for the Deal, Jug Bay, and Eastern Neck sites. The Deal site was sampled for five data points. The duration of the experiments was >200 days for all incubations except for the Deal samples, which were incubated for 94 days. The number of incubated vials totaled 22, 16, 6, and 6 including all sites and depths at Blackwater, Eastern Neck, Jug Bay, and Deal Island, respectively. Although samples for the chemical analysis of nutrients (NH_4^+, NO_x^-, soluble reactive P) and dissolved inorganic C (DIC) were collected during the time course, these data did not resolve changes sufficiently against high background values and these data are not reported here. This sampling, as well as the oxygen and pH measurements, took place after the vials were allowed to settle the particulate material, minimizing the removal of particulates. With the depletion of oxygen and removal of water, the aerobic experiments were not a “continuous incubation” and rates were determined via regression for time periods that were initially short (~10–12 days) to >60 days as rates slowed down. The interval length was based on the amount of oxygen depletion. After two or three sample collections, the volume of removed water was replaced with low nutrient concentration water of the same salinity within the vial and oxygen was introduced into the jar headspace. Because of iron sulfide oxidation and sulfuric acid production, we added dilute NaOH to the jars to maintain pH when pH dropped to less than 6; this was necessary because most water was carried over between water additions. The values of pH in some cases decreased to <4 prior to neutralization. The oxygen concentrations were determined on aqueous samples, so the total oxygen in the jar was determined from the volume of water and air and a temperature and salinity Henry’s law coefficient. The statistical presentation of results uses medians and means (±S.D.).

RESULTS

Solid Phase Analyses — Decomposition Experiments

The concentration of solid phase organic carbon ranged from 2.3% to 41.1%, averaging 21.0 ± 13.1% (Figure 3). The lowest concentrations were obtained from the three Jug Bay samples plus a coarse-grained surface sample (Eastern Neck-2A) derived from beach over wash. The Jug Bay core location represents a depositional environment with high inputs of riverine-derived inorganic particles; previous observations suggest that some sites may have higher organic matter concentrations (Merrill 1999). In core BW-1, the bottom (56–79) section consisted of fine-grained inorganic particles with much lower carbon content than the sections above. Core BW-2 showed a similar profile. The Deal Island core had consistently high organic carbon throughout. Solid phase nitrogen concentrations (Figure 3) generally mirrored those of the organic carbon, ranging from 0.16% to 2.27% and averaging 1.21 ± 0.69%. The solid phase C and N concentrations were used to estimate the nitrogen or carbon-specific decomposition rate (day^{-1}). The regression of C to N in our sample set (Figure 4a) yielded a molar ratio of 20.9, with average molar C:N ratios of 19.1 ± 4.4 (Figure 4b). The N:organic P molar ratio averaged 55 ± 23. The organic carbon to organic phosphorus molar ratio averaged 1,110 ± 590.

Because the pH of the samples decreased and continually changed as a result of pyrite oxidation, the estimation of the total amount of dissolved inorganic carbon in the vials was not reliable. Consequently, O_2 consumption was used as a proxy for organic matter mineralization, assuming a 1:1 ratio between oxygen uptake DIC production. Oxygen depletion is shown for four time periods for a sample from BNWR, with Figure 5a showing a typical time course. Oxygen depletion was followed by reaeration prior to the start of a new sampling interval. The rates of oxygen depletion decreased throughout the incubation period, with average rates for all BNWR sites of ~1 µmol/g/day at the end of the incubation (Figure 5b). The decay rate was based on the oxygen depletion and the solid phase carbon concentration. The decomposition rates at BNWR decreased over time from rates of $0.00058 \pm 0.00048\ \text{day}^{-1}$ during the first 14 days to $0.00006 \pm 0.00002\ \text{day}^{-1}$ by the last time period, a factor of 10 decrease (Figure 5c). This large decrease over time likely reflects the chemical oxygen demand from the oxidation of iron sulfide minerals:

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4. \quad (1)$$

Thus, the oxidation of 1 μmol of pyrite sulfide consumes 1.875 μmol of oxygen. Considering all of the data from all sites and using Equation (1) with the CRS data, we observed that the potential oxygen uptake in the first three time intervals of oxygen uptake was ≤ potential sulfide oxidation in 14 of 19 time courses. The initial rates are thus influenced by sulfide oxidation and we use the fourth interval for discussion here, recognizing that initial rates could be higher if sulfide oxidation was incomplete, and lower if sulfide oxidation persisted. Overall, the rates of organic matter decay were in the range of 0.00005 to $0.0001\ \text{day}^{-1}$ for all of the sites (Figure 6). These estimates increase by up to two-fold if sulfide oxidation is not included. The estimate of N mineralization from Deal Island was $0.00006 \pm 0.00003\ \text{day}^{-1}$, similar to the oxygen-based, sulfide corrected rate.

Sediment N and P Burial Rates

Three systems had especially good spatial coverage and multiple data points for estimating the rates of N and P burial (Table 1; Figure 7). The rates of N burial averaged 10.6 ± 6.1, 21.2 ± 10.6, and 16.9 ± 11.9 g N/m^2/year for Monie Bay, Choptank River, and Patuxent River wetlands, respectively, with the standard deviation ranging from 50% to 70% of the mean rate. In Patuxent River tidal wetlands, Merrill (1999) apportioned the N burial rates into

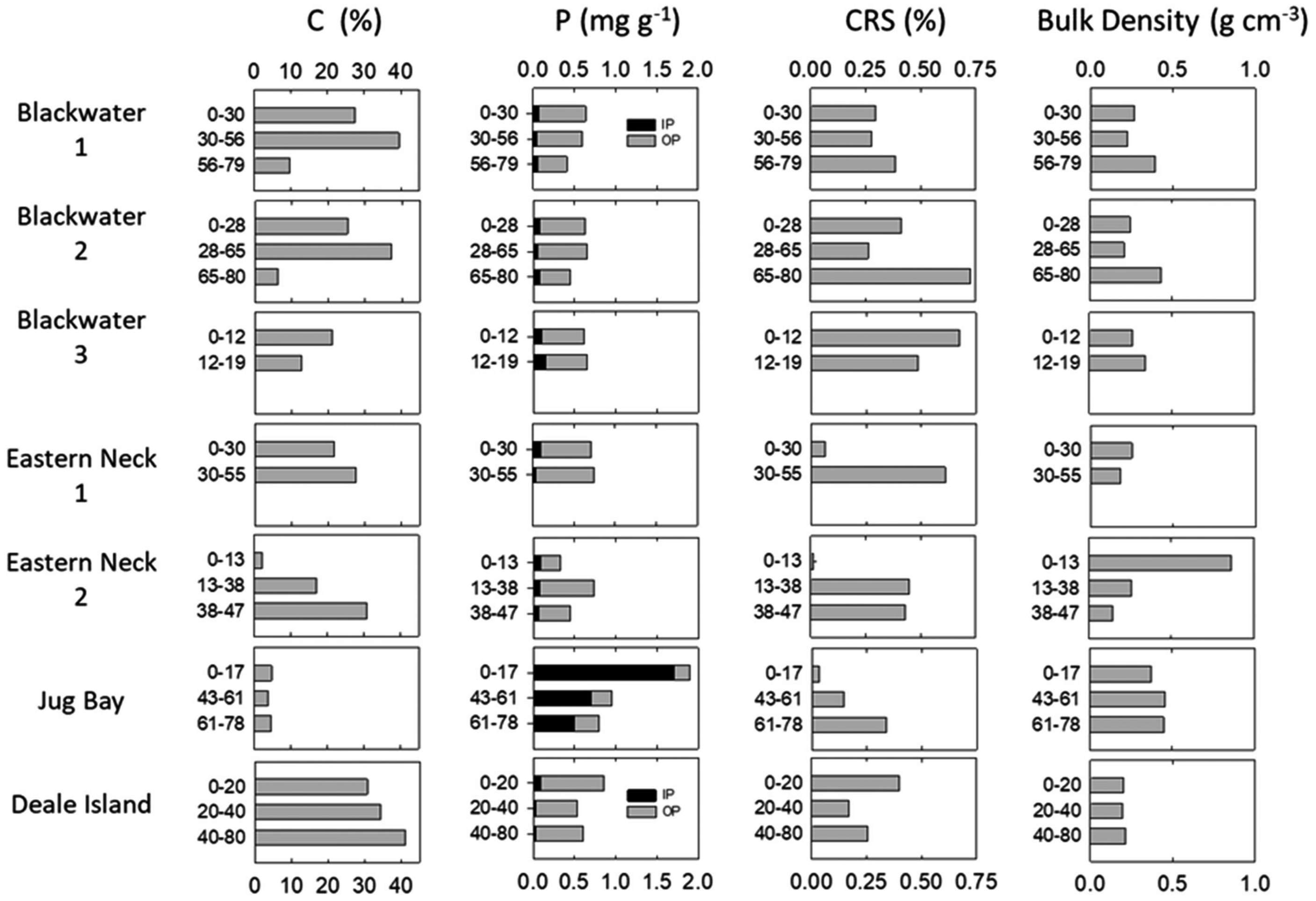

FIGURE 3. Sediment composition of samples used for sediment decomposition rates. The depth intervals (cm) are shown at the left of the boxes and data are shown for percent C, inorganic (IP), and organic P (OP) summing to total P, chromium reducible sulfur (CRS), and bulk density.

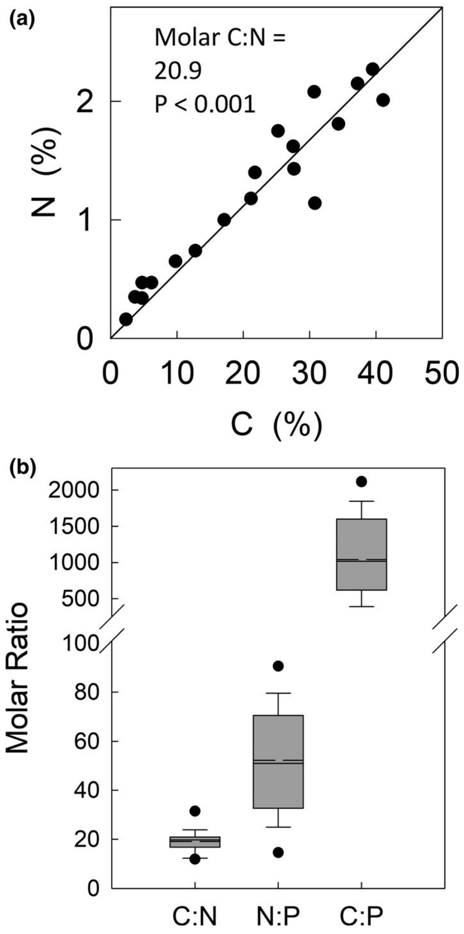

FIGURE 4. Regression of N vs. C in all sediment samples ($R^2 = 0.916$) used for decomposition studies (a) and box plots of the ratios of C:N, N:P, and C:P where P is organic P (b). The solid line is the median and the dashed line is the mean, the boxes define the 25th–50th and 50th–75th percentile of the data, the bars represent the 10th–25th and 75th–90th percentile of the data, and the dots are outliers. All data are on a mass basis and 19 soil samples from different sediment depth intervals are represented throughout.

plant communities, and when accounting for the area of each plant community, showed N burial rates of 18.3 g N/m^2/year, similar to the average rates. The N burial rate for Poplar Island is estimated from the C burial rate of 206 g C/m^2/year (Staver et al. 2020) using the average molar C:N ratio observed in our decomposition studies (19.1). The Poplar Island N burial rate is reflective of short-term N burial after wetland creation and may overestimate long-term burial. However, Poplar Island N burial rates are similar to our mesohaline rates and somewhat lower than observations for tidal fresh areas. Average P burial rates varied widely, ranging from low rates (0.63 ± 0.38 g/m^2/year) in Monie Bay marshes to very high rates in the Patuxent River marshes (4.26 ± 3.88 g/m^2/year). Merrill's (1999) estimate of Patuxent marsh P burial rates normalized to the area of the plant community was 3.13 g P/m^2/year, a rate 27% lower than the average rate.

Denitrification Rates

Denitrification rates, estimated as the net efflux of N_2-N, were of a similar magnitude as N burial rates (Table 1). The studies summarized here reflect different degrees of spatial and temporal coverage, but all utilize the N_2:Ar approach to measuring denitrification. The Patuxent measurements were seasonal and encompassed two sites, whereas the Sassafras River data were a single suite of measurements at four sites in early autumn. Denitrification rates from the created wetlands at Poplar Island are from the summer of the second year of marsh development after exposure of the soils to tidal inundation. Dark and illuminated incubations generated daily rates that were extrapolated to annual rates (Figure 8). The mean rate (16.2 ± 6.6 g N/m^2/year) was similar to observations at other Chesapeake Bay sites. These summer rates may be an overestimate of denitrification when extrapolated to the whole year.

DISCUSSION

Nutrient Sequestration in Northern Chesapeake Tidal Marshes

The N and P burial rate estimates in Table 1 compare well with other measurements made on the United States (U.S.) East Coast. The N burial rates from this study (10–21 g N/m^2/year) are similar to values from mid-Atlantic tidal fresh-water/oligohaline wetlands (Hudson River, Lower Chesapeake Bay) and somewhat higher than the observations in Massachusetts and Georgia (Megonigal and Neubauer 2019). Salt marsh N burial rates in Barnegat Bay, New Jersey (Velinsky et al. 2017) averaged about half of Monie Bay rates, while the wastewater-impacted Murderkill River in Delaware showed decreasing N burial toward the saltwater end member (Velinsky et al. 2020). Our P burial rates were similar to observations in coastal New Jersey and Delaware (Velinsky et al. 2017, 2020) and a number of tidal fresh-water and oligohaline sites (Megonigal and Neubauer 2019).

Although the denitrification rates in Table 1 reflect identical measurement procedures, the number of sites and temporal coverage were very different. Overall, these rates are consistent with other estuarine ecosystem measurements using the N_2:Ar approach (Elsey-Quirk et al. 2013). Although many

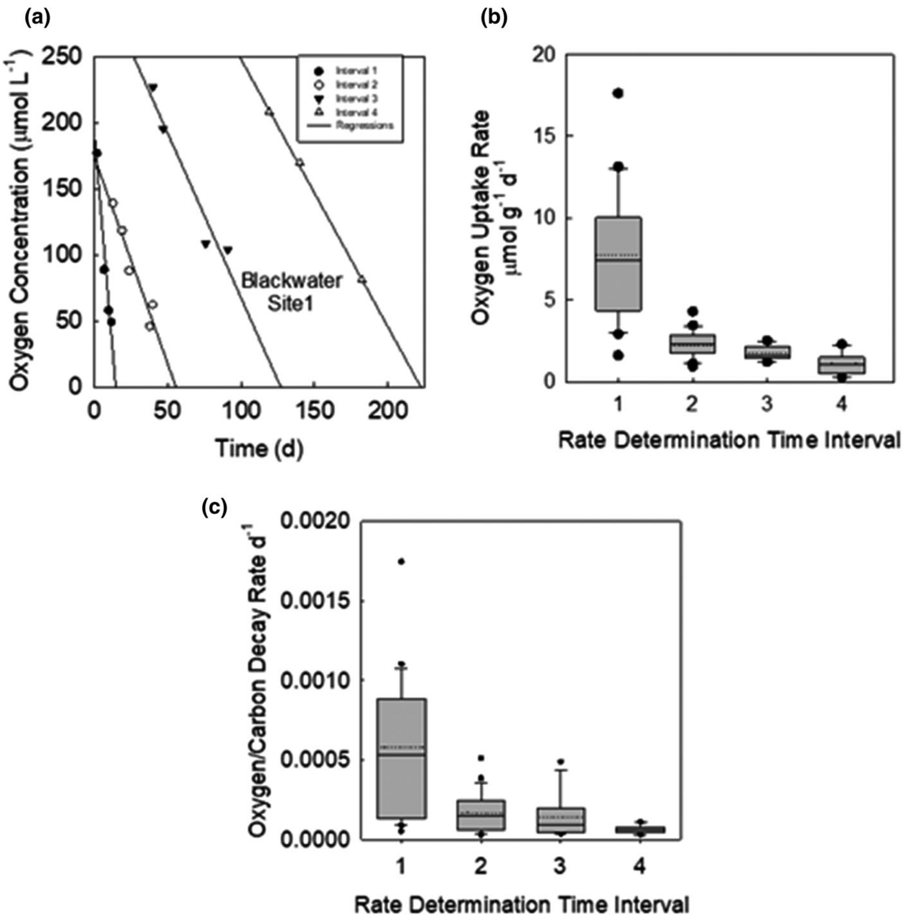

FIGURE 5. Panel a presents a representative time course of oxygen depletion from a single Blackwater National Wildlife Reserve (BNWR) sample. Panel b is a box plot of oxygen uptake rates over time for all samples from BNWR. Panel c presents decay rates in inverse days. In Panels b and c, the box plots are all rates for the time period 2–12 days of incubation (Time 1), the period 13–40 days (Time 2), the time period 40–91 days (Time 3), and the period 119–182 days. The solid line is the median and the dashed line is the mean, the boxes define the 25th–50th and 50th–75th percentile of the data, the bars represent the 10th–25th and 75th–90th percentile of the data, and the dots are outliers.

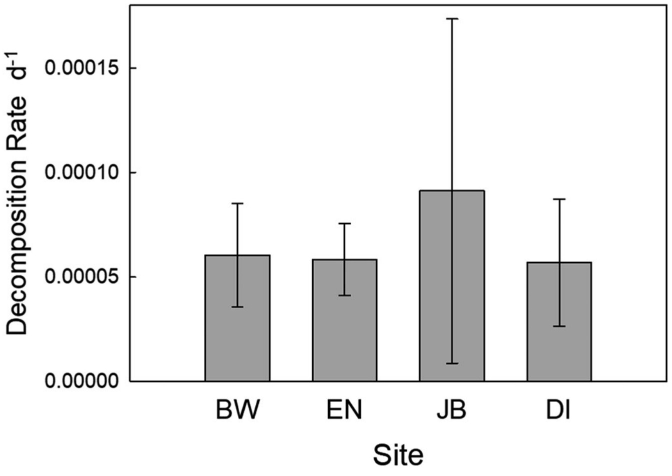

FIGURE 6. Average (±S.D.) decay coefficients from aerobic experiments in four Chesapeake Bay marsh systems.

studies use the acetylene block approach to estimate denitrification (van Raalte and Patriquin 1979), rates from slurried sediments are likely not representative of environmental rates and even with intact cores, coupled nitrification–denitrification is not included (Cornwell et al. 1999).

The ratios of organic C, N, and organic P may be useful for determining the source of the organic matter found in sedimentary deposits (Thornton and McManus 1994), though isotopic evidence may provide a better idea of organic matter provenance (Bianchi 2007). The observed ratios are consistent with wetland plant organic matter, without a large algal component. The elevated inorganic P concentrations in the Jug Bay core are consistent with a large input of inorganic particles from a tidal river that is extremely high in suspended sediment and with inputs both from agriculture and wastewater (Jordan

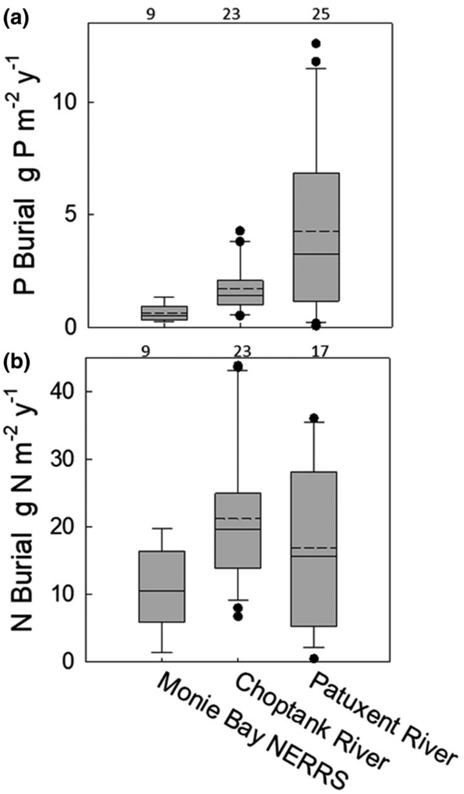

FIGURE 7. Nitrogen (a) and P (b) burial rate box plots from three wetland systems in the upper Chesapeake Bay. The numbers at the top of each box indicate the number of observations. The solid line is the median and the dashed line is the mean, the boxes define the 25th–50th and 50th–75th percentile of the data, the bars represent the 10th–25th and 75th–90th percentile of the data, and the dots are outliers.

et al. 2008). Suspended sediment composition in the main branch of the upper Patuxent River averaged 1.9 mg/g inorganic P, similar to the concentration (1.7 mg/g) observed in the upper core horizons in subtidal sediments. The down core decrease in inorganic P occurs as the concentration of CRS increases, suggesting that the loss is associated with conversion of iron oxide minerals to iron sulfide minerals, resulting in the release of inorganic P (Roden and Edmonds 1997).

Changes in Nutrient Retention with Erosion

The aerobic decomposition rates of these wetland soils under our experimental conditions were relatively slow, suggesting that the organic matter was relatively recalcitrant, as expected from peat sediment decomposition experiments elsewhere (Moore and Basiliko 2006). The decomposition decay coefficients (0.00005–0.0001 day^{-1}) compare well with the observations of peat degradation in peat bogs of NW Europe, with Brouns et al. (2014) observing decay rates of 0.0001 day^{-1}. Most organic degradation studies in wetlands involve litter decomposition; in tidal wetland profiles, sediment accretion rates typically are ~30–50 cm per century (Craft et al. 1993; Neubauer 2008), so much of the material eroded from wetlands is subject to mineralization over decades. Litter bag studies of tidal Chesapeake wetland soils and plant material generally have much higher decay estimates than suggested here (Kirwan and Blum 2011; Kirwan and Megonigal 2013).

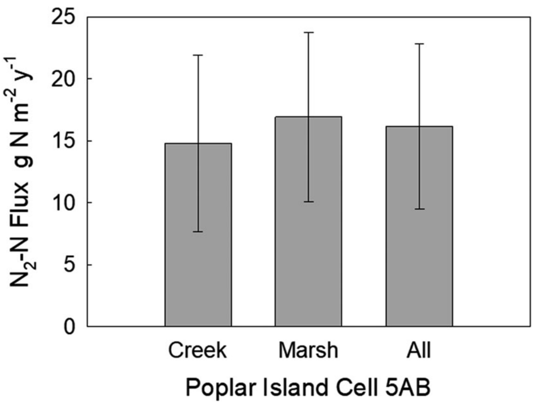

FIGURE 8. Average rates of denitrification (±S.D.) at Poplar Island extrapolated from summer 2019 to a whole year, with estimates based on dark-only incubations plus light-only incubations, with a daily rate that utilized day-length for estimation. The creek data are based on four observations from marsh creeks while the marsh observations are based on seven marsh cores.

The construction of mass balance estimates for coastal ecosystems often utilizes data sources of varying quantity and quality, illustrated by the Chesapeake Bay-wide mass balance presented in Boynton et al. (1995). Here, we utilize all available data for the purpose of generalizing rates of denitrification and the burial of N and P, recognizing the limitations of the data for a mass balance and presenting an emphasis on the data ranges. For N and P burial, only the data at Monie Bay are representative of mesohaline conditions, with the Choptank River and Patuxent River data most representative of tidal fresh-water and oligohaline marshes. For denitrification, most information is from tidal fresh environments, with the exception of Monie Bay and Poplar Island. In the Monie Bay wetland ecosystem, sediment organic matter concentrations were considerably higher than in the Choptank and Patuxent, and as a consequence, bulk density in that ecosystem was much lower.

The erosion of wetland soils yields total nitrogen, with the marsh loss area multiplied by the N inventory estimated from vertical profiles (Table 2) providing an estimate of the total N exported from the marsh (Equation 2). The two deep cores from BNWR had a peat layer over inorganic soils and the inventory from those two sites with peaty soils had a similar inventory as Deal Island, with the three cores averaging 32,074 ± 590 kg N/ha; for calculation purposes, we used 32,074 kg N/ha as our high value. The other core N inventories ranged from 5,462 to 9,768 kg N/ha, with 8,500 kg/ha/year used to represent lower inventory sites. There are a broad range of estimated past and future wetland loss rates available for the region (Glick et al. 2008; Stubbs et al. 2020), with higher loss rates suggesting future projections of ~1% marsh loss per year in tidal wetlands. Wetland loss is highly variable and for contrast, we also used a much higher 4% annual rate of marsh loss to illustrate loss in a highly degraded wetland. The estimation of total N export may thus be estimated:

$$\mathrm{TN}_{\text{eroded mass}}(\text{kg/year}) = \mathrm{N}_{\text{Inventory}}(\text{kg N/ha}) \times \mathrm{A}_{\text{Marsh Loss}}(\text{ha/year}). \quad (2)$$

Ultimately, the export of the N is of water quality concern if biologically reactive N forms are released and can be utilized for algal growth. The eroded N likely has highest decay rates under the aerobic conditions under which we incubated our sediments. Using the sulfide oxidation-corrected decay coefficients, we estimated that the total lability would be <3.3% of the total N. Also shown are the decay coefficients that would be calculated if sulfide oxidation was ignored, providing an upper limit for decomposition. While sediments may be suspended in the water column for weeks prior to burial (Sanford 1992), upon deposition they can be buried or mixed (Rice 1986) into anoxic sediment horizons (Kemp et al. 1990). The typical 3–6 mm/year bottom sediment accretion rate (Officer et al. 1984) is sufficient to bury sediment into anaerobic horizons within a year. We used the time frame of one year in which we assume the particulate N remains aerobic and reactive.

The calculation yields a reactive N-eroded mass each year:

$$\text{Eroded N}_{\text{Reactive}}(\text{kg/ha/year}) = \mathrm{TN}_{\text{eroded mass}}(\text{kg N/ha/year}) \times \text{Reactivity Coefficient}(\text{year}^{-1}) \times \text{Period of reactivity } (y). \quad (3)$$

Figure 9a shows the range of TN export rates expected with low and high erosion rates and inventories, with TN export rates of 85–321 kg N/ha/year for a 1% year^{-1} marsh loss rate and 340–1,283 kg N/ha/year for a 4% year^{-1} marsh loss rate. Using the higher sulfide-corrected annual labile production (0.033 year^{-1} for one year) and a marsh area of 1 ha, we estimate labile N release rates of 2.8–10.6 and 11.2–42.3 kg N/year for 1% and 4% marsh loss, respectively (Figure 9b).

TABLE 2. Data used for N and P calculations in discussion. Decay coefficients are presented as both the sulfide-corrected and non-sulfide-corrected rates.

	Unit	Low	High
Denitrification	kg N/ha/year	100	220
N Burial	kg N/ha/year	100	220
P Burial	kg P/ha/year	6	38
Decay including sulfide oxidation	day^{-1}	0.000061	0.000091
Decay including sulfide oxidation	year^{-1}	0.021	0.033
Decay without sulfide oxidation	day^{-1}	0.000074	0.00021
Decay without sulfide oxidation	year^{-1}	0.027	0.074
Vertical N Pool	kg/ha	8,500	32,074
Vertical OP pool	kg/ha	56	106
Vertical IP pool	kg/ha	12	204
Vertical TP pool	kg/ha	117	260
Wetland areal loss	%	1	4

The other key term is the effect of the loss of area in which denitrification and burial occur (Equation 4). This term does not include adding new marsh via transgression (Schieder et al. 2018) and represents loss without replacement. The remaining N retention is directly related to the proportion of marsh remaining.

$$\text{Remaining N retention kg N/ha/year} = (\mathrm{N}_{\text{denitrification}} + \mathrm{N}_{\text{burial}} \text{ kg N/ha/year}) \times \text{proportion of remaining marsh}. \quad (4)$$

The annual change in continuing N retention (Figure 9c) for low and high burial retention with 1% and 4% marsh loss rates are of a similar order but generally less than the amount of labile N released by erosion. The N ecosystem services, expressed on the basis of the area of the original marsh, may be calculated as the remaining N retention in remaining marsh minus the release of reactive N.

$$\mathrm{N}_{\text{ecosystem services}}(\text{kg N/ha/year}) = \text{Remaining N retention} - \text{Eroded N}_{\text{reactive}}(\text{kg N/ha/year}). \quad (5)$$

With these equations, a linear decrease in the ongoing N retention and the nitrogen ecosystem service value can be shown over time (Figure 10a), with

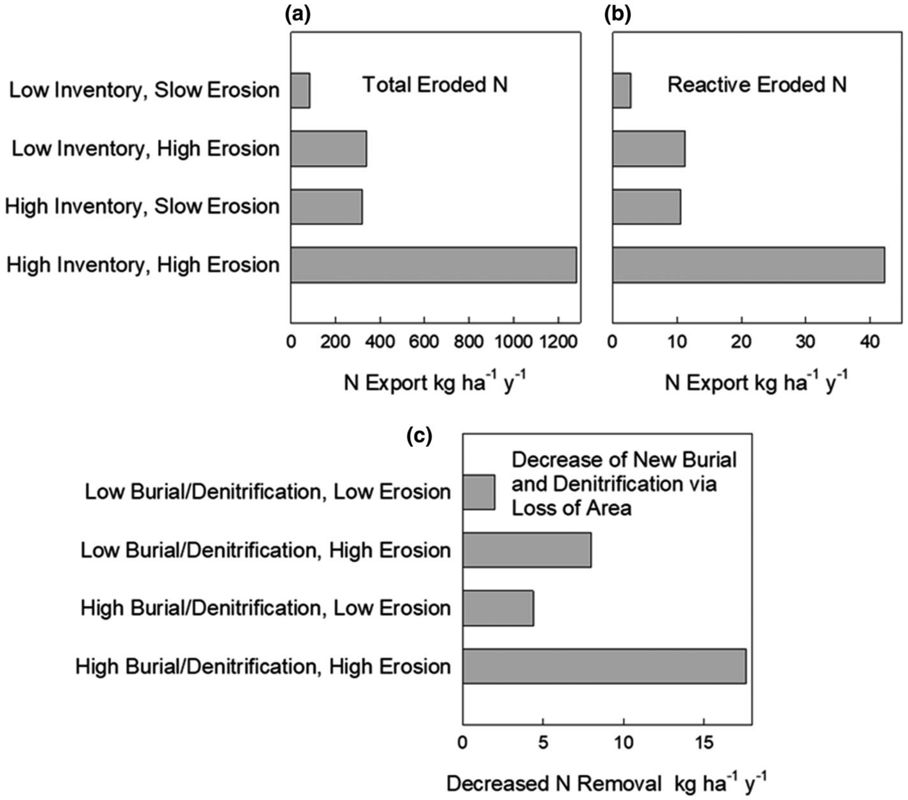

FIGURE 9. Bar graph of total N erosion (a) and the reactive N erosion (b) for low and high N vertical inventories and low (1% year^{-1}) and high (4% year^{-1}) wetland loss rates. Panel c shows the change in N retention with low/high wetland loss rates and low/high denitrification plus N burial rates.

the difference between ongoing retention and the net value being the release of labile N with erosion. Two contrasting N balances are presented: a low initial ecosystem service scenario with low rates of denitrification + burial (200 kg/ha/year), inventory (8,500 kg/ha), and marsh loss (1%) and a scenario with high denitrification + burial (440 kg/ha/year), inventory 32,074 kg/ha, and erosion 4%. The low rate case of erosion, burial + denitrification and inventory shows relatively little loss of net N retention over 25 years, while the high erosion case with high nutrient retention had a near total depletion of value in <25 years, the point at which the whole marsh disappears. The actual changes in a given marsh segment can only be estimated if solid phase nutrient content, burial rate, denitrification, and N inventory are assessed. A 10-year cumulative effect of different rates of erosion and inventories (Figure 10b) show differences between N removal in a no-loss intact marsh and both ongoing and net ecosystem N removal.

For examination of changes in P removal, both the organic P and inorganic P components of the soils must be considered. The erosion of organic P is treated similar to the erosion of N (Equation 6), with an estimate of the eroded mass from the organic P inventory and the production of reactive P related to the decomposition coefficient (Equation 7), assumed to be similar to N (0.033 year^{-1}). As with N, the decrease in ongoing sedimentation plus the release of reactive P reflects the change in nutrient ecosystem services (Equation 8).

$$\begin{aligned}&\mathrm{OP}_{\text{eroded mass}}(\text{kg P/ha/year}) =\\ &\mathrm{OP}_{\text{Inventory}}(\text{kg P/ha}) \times \mathrm{A}_{\text{Marsh Loss}}(\text{ha/year}),\end{aligned} \qquad (6)$$

$$\begin{aligned}&\text{Eroded } \mathrm{OP}_{\text{Reactive}}(\text{kg/ha/year} =)\\ &\mathrm{OP}_{\text{eroded mass}}(\text{kg P/ha/year})\\ &\times \text{Reactivity Coefficient}\left(\text{year}^{-1}\right)\\ &\times \text{Period of reactivity (year)},\end{aligned} \qquad (7)$$

$$\begin{aligned}&\mathrm{OP}_{\text{ecosystem services}}(\text{kg N/ha/year}) =\\ &\text{Remaining P retention}\\ &-\text{Eroded } \mathrm{OP}_{\text{reactive}}(\text{kg P/ha/year}).\end{aligned} \qquad (8)$$

Using the OP inventories and burial rates from the Patuxent core (557 kg/ha; 8.06 kg P/ha/year) the

OP ecosystem service rates decreased largely according to the rate of marsh loss (Figure 11c,d). The OP fraction of total P was 21%, with the reactivity of inorganic P being a potentially larger source of reactive P to the estuary. The eroded mass of IP is calculated in Equation (9), with the reactive proportion of the IP pool estimated in Equation (10).

$$\mathrm{IP}_{\text{eroded mass}}(\text{kg/ha/year}) = \mathrm{IP}_{\text{Inventory}}(\text{kg P/ha}) \times A_{\text{Marsh Loss}}(\text{ha/year}), \quad (9)$$

$$\text{Eroded } \mathrm{IP}_{\text{Reactive}}(\text{kg/ha/year}) = \mathrm{IP}_{\text{eroded mass}}(\text{kg P/ha/year}) \times \text{Reactive Proportion.} \quad (10)$$

The IP inventory (2,041 kg P/ha) and burial rate (29.5 kg/ha/year) for the Patuxent decreased with increasing reactivity. Although the release of inorganic P from particulates has not been directly estimated, some bounds on this process may be made. In the Patuxent River, sediment inorganic P concentrations decreased ~42% from the fresh-water input to the mesohaline part of the estuary (Jordan et al. 2008) due to P efflux from sediments after loss of iron oxide adsorbing surface area. Li et al. (2015) suggest that Fe-associated P can be buried in sulfidic Chesapeake sediments. In the upper Chesapeake Bay, ~1/4 to 1/3 of inorganic P from fluvial inputs may be solubilized when exposed to hydrogen sulfide (Vulgaropulos 2017) such as found in mid-bay sediments (Cornwell and Sampou 1995). With potential desorption of inorganic P from iron oxides occurring across the salinity gradient, as well as across the vertical redox gradient within sediment profiles, we suggest that it is likely that the potential lability of inorganic P is considerably <25%. The effect of the reactivity used is large, particularly with high erosion rates (Figure 11a,b). The sum of the two P pools (Figure 10 d), expressed as a net P ecosystem service, is driven by the larger pool. For the oligohaline/mesohaline peat sites, we would expect that the small IP pool size and the likely presence of anoxic/sulfidic conditions would make the IP pool largely unimportant to the net change in ecosystem services.

Examination of Assumptions

A series of assumptions are implicit in this analysis and their consideration is necessary to evaluate the strength of this study's conclusions. This analysis of nutrient balance depends on data from many sources, and for processes such as denitrification and organic matter decomposition, spatial variability within wetlands is not addressed. If quantification of the nutrient balance for a single wetland segment is important, all elements of the balance need to be addressed with sufficient spatial coverage to ensure the best estimates. This could be particularly important if monetary values of ecosystem services are considered in management decision-making.

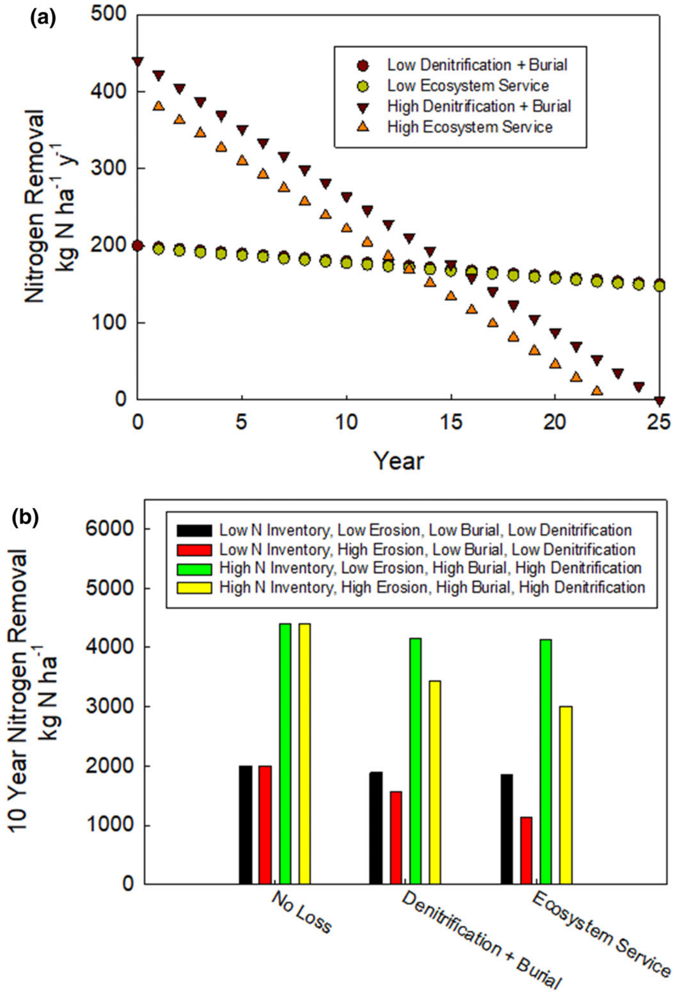

FIGURE 10. Plot of nitrogen removal in tidal marshes over time (a) for yearly denitrification plus nutrient burial in marshes with low denitrification, burial, inventory and marsh loss, marshes with high values of these same parameters, and the net ecosystem N removal which includes erosive inputs of reactive N that are released to the estuary. Plot b shows the cumulative nitrogen removal for 10 years with different denitrification + N burial rates (200 and 440 kg N/ha/year), vertical inventory (8500 and 32,074 kg N/ha), and erosion rate (1% and 4%).

Data Assembly for Nutrient Burial, Denitrification, and Decomposition Studies. The data used in this study are derived from 10 different sites, with only the upper Patuxent marshes having the data for all the elements of this analysis. There are relatively few data for denitrification for brackish marshes in upper Chesapeake wetlands, with these data skewed toward nitrogen-enriched tidal fresh and oligohaline marshes. The inventories of N and organic P at BNWR and Deal Island are likely similar to the mesohaline marshes at Monie Bay, and the low P burial at Monie Bay may be relevant to BNWR and Deal Island. For sites with similar organic composition, wetland accretion that matches relative sea-level rise constrains the rate of N and organic P burial, with changes in bulk density having the biggest effect on mass fluxes. Because of the "mismatch" of data, we have presented an unusually broad range of rates and inventories here.

Rates of Wetland Loss. A full analysis of all the studies on past and future wetland loss and transgression is beyond the scope of this paper. We have use an idealized 1.0-ha marsh as an example for calculation purposes, recognizing that large tracts of wetland have minimal losses and that other wetlands are disappearing rapidly. Most marsh loss studies use inventories of wetland area over time, with variable levels of resolution. Wetland transgression into upland areas may help maintain wetland areal coverage, but some wetlands cannot migrate because of steep local elevations or engineered barriers to migration.

Reactive N Release from Eroded Sediments. The decomposition coefficients of this study are consistent with aerobic degradation observed in

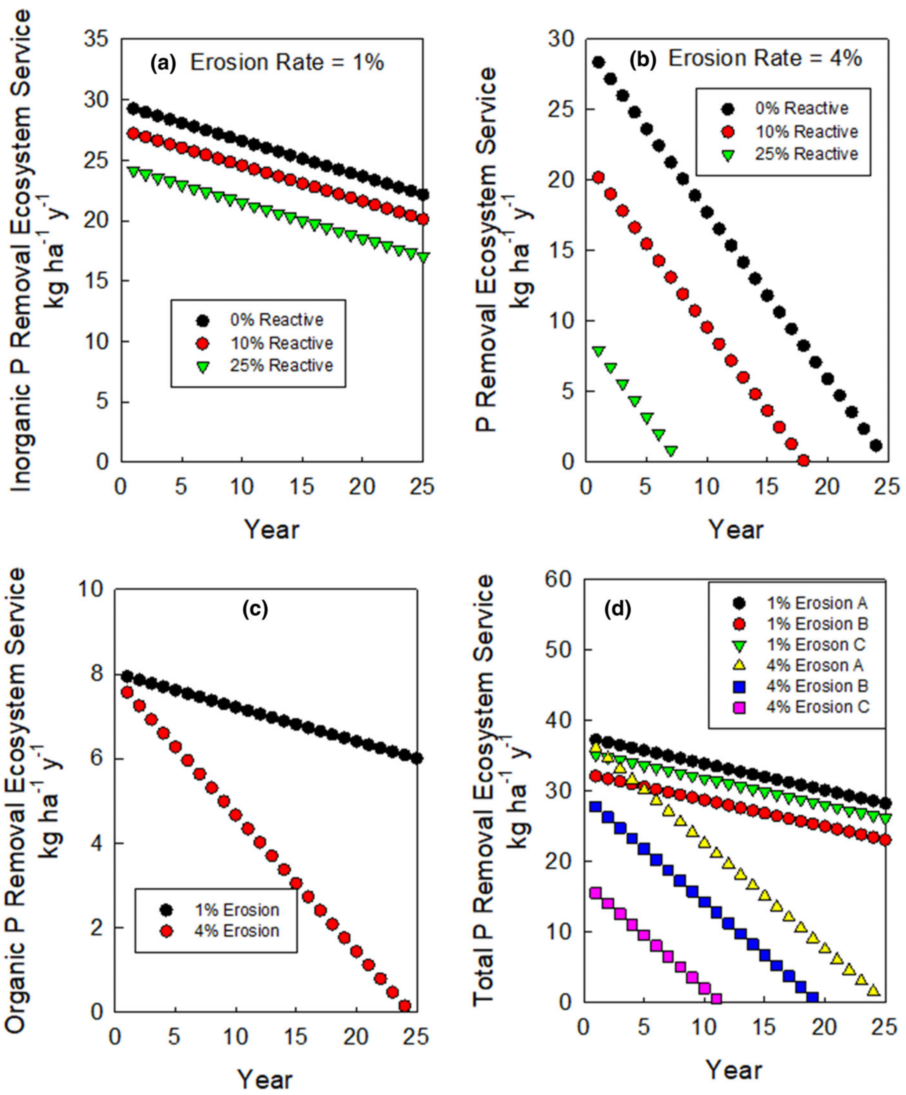

FIGURE 11. Changes in inorganic, organic, and total P removal by tidal wetlands. The data here uses inventories and burial rates from the upper Patuxent River. Panels a and b show the loss of P removal ecosystem services with 1% erosion and 4% erosion. Panel c shows the effects of erosion on the removal of organic P, and panel d shows the loss of P removal nutrient services with two rates of erosion and three levels of IP reactivity (A = 0%, B = 10%, and C = 25%).

other peat degradation studies. The aerobic release of N may be less than that predicted from O_2-based decomposition, with reincorporation in bacteria and bacterial degradation products enhancing retention (Schlesinger and Bernhardt 2020). However, we have limited our estimate of release of N from eroded particulates to a time period of one year, assuming that the particulate N is buried or mixed into anaerobic sediments and that future reactive N releases are minimal. This suggests that ~97% of this material remains unreactive. Given the range of biogeochemical conditions in Chesapeake Bay sediments, including the presence/absence of illumination, oxygen, and animal ingestion, the potential release of reactive N could be different than these projections.

Reactive P Estimates. The conversion of organic P from eroded wetland particulates to reactive inorganic P is treated similar to the mineralization of marsh N, recognizing that incorporation into bacteria may result in an organic P pool that is more refractory (Ingall and Cappellen 1990). The treatment of inorganic P, however, has very different environmental controls. The down core increase in CRS in the Patuxent core, generally associated with the production of iron sulfide minerals, coincides with the decrease in inorganic P (Figure 3). The much higher concentrations of inorganic P in the upper Patuxent River are related to local inputs from the watershed (Boynton et al. 2008; Jordan et al. 2008). The production of iron sulfides from iron oxides results in the release of Fe-bound inorganic P; iron sulfide minerals have much lower adsorption coefficients (Krom and Berner 1980). In the Chesapeake Bay and its tributaries, inorganic P in bottom sediments is most often associated with the cycling of Fe oxides (Hartzell et al. 2010; Li et al. 2015). The potential mobility of deposited inorganic P, particularly the Fe-bound component, is generally related to salinity and oxygen concentration (Caraco et al. 1990; Kemp et al. 2005), with both affecting inorganic P release from Fe oxides (Lehtoranta et al. 2009). Thus, the potential release of inorganic P from eroded marsh soils is not solely related to its association with Fe within the marsh; the biogeochemical characteristics of the sedimentary environment into which it is exported will have a large effect on inorganic P mobility. Consequently, the characterization of inorganic P alone in a marsh may be insufficient to predict the production of dissolved inorganic P after deposition in the estuary. The high estimate of 25% mobility used as an example here may be representative of the mobility of watershed materials freshly deposited from the watershed, but is likely a vast overestimate of mobility in marsh soils in which diagenetic processes remobilize the most reactive fractions.

Settlement of Eroded Particles on Marshes. Particles eroded from marshes can also be deposited back onto the marsh. In a macro-tidal estuary, carbon isotopic evidence revealed that marsh edge erosion was an important source of mass to maintain the marsh platform elevation in the face of sea-level rise (Hopkinson et al. 2018). For a net N balance, understanding this input of eroding marsh particles is important to not overestimate "new" burial of N within the marsh, or overestimating the export of N to the estuary.

Mass Balance Estimate

A simple mass balance calculation can be made to determine if these changes in marsh acreage merit concern for Chesapeake Bay water quality. If we consider the acreage of tidal marsh in the northern Chesapeake (Maryland, 94,128 ha; Clearwater et al. 2000), the proportion of tidal marsh that is brackish or salt (98% from Glick et al. 2008) and likely peaty, we suggest that the nutrient balance is most affected by sites such as Monie Bay, BNWR, and Deal Island. Using (1) 1% year^{-1} marsh loss, (2) the inventories for N and P from peaty sediments, (3) the proportion of P that is OP (87.7%), and (4) the rate of N and organic P burial at Monie Bay, assuming IP is unreactive, we estimate the sum of reactive N/P release in these Maryland tidal marshes plus lost trapping to be 197,553 kg N/year and 8,796 kg P/year. This represents 0.17% of P loading and 0.22% of P loading into the northern Chesapeake Bay (Boynton et al. 1995). These numbers are directly scalable to the amount of each ha that is eroded; 0.5% year^{-1} erosion rates would halve these proportions. In tidal fresh-water marshes, the much higher concentrations of inorganic P could result in a higher release than observed in mesohaline marshes. At the whole Chesapeake Bay scale, these proportions appear low; however, within tributaries and smaller embayments, marsh erosion could constitute an important change in N or P balances. If the total loss of N and P had been considered without regard to the lability of the organic matter, the proportion eroded N and P would be 2.6% and 2.5% of upper bay N and P loading, respectively. Additions of marsh acreage, such as at Poplar Island where dredging activities have provided an opportunity for wetland creation, have the potential to mitigate a small proportion of the nutrient ecosystem function losses. However, the transgression of wetlands landward, such as proposed by Schieder et al. (2018), represents a potentially large means to maintain wetland ecosystem functions.

SUMMARY AND CONCLUSIONS

Wetland soils in the upper Chesapeake Bay serve an important role in the removal of N and P from tidal waters (Merrill and Cornwell 2000; Boynton et al. 2008). The burial of N and P can cease with marsh loss, and result in the reintroduction of marsh soils into subtidal environments. This potential lack of permanence can be an issue in net N and P balances if the exported wetland soils result in release of labile N and P to fuel ongoing eutrophication. Conversely, the N removal via denitrification represents the most permanent form of removal.

This analysis is limited by the lack of spatial coherence of the different studies; detailed work on a single system, with substantially more temporal coverage, would provide a more precise mass balance of N and P in these accreting and eroding wetland ecosystems. However, these data nevertheless show that the main biogeochemical consequences of losing marsh acreage is not the addition of eroded marsh N and P to the Chesapeake Bay, but instead points to the loss of enhanced denitrification and ongoing nutrient burial. Adding marsh acreage, such as at Poplar Island, has the potential to mitigate the loss of this ecosystem function. The transgression of wetlands landward, such as proposed by Schieder et al. (2018), represents another mechanism to maintain wetland ecosystem functions.

Little is known about how quickly the ecosystem functions that benefit water quality are established in transgressing marshes, a subject that merits future study. The rate of establishment of nutrient removal functions will have a substantial bearing on the value of wetlands under climate-related stress. In addition, more realistic experiments on the fate of marsh particulates in estuarine bottom sedimentary environments would better constrain the inputs of N and P to the Chesapeake Bay. Changing redox, ingestion by benthic animals, and variable time in the water column may influence nutrient regeneration; postdepositional processes such as denitrification and adsorption of inorganic P to particles will likely attenuate impacts. However, the processes described in this analysis can form the basis of better assessments of the biogeochemical consequences of marsh loss.

DATA AVAILABILITY STATEMENT

The data used in this publication were assembled from journal publications, theses, and both published and unpublished reports that span 25 years. The authors will provide electronic copies of the reports and theses upon request.

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AUTHOR CONTRIBUTIONS

Jeffrey C. Cornwell: Conceptualization; Funding acquisition; Project administration; Visualization; Writing – original draft. **Michael S. Owens:** Data curation; Methodology; Writing – review & editing. **Lorie W. Staver:** Conceptualization; Funding acquisition; Project administration; Writing – review & editing.

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