Shifts in the relative availability of phosphorus and nitrogen along estuarine salinity gradients

Jeanne L. Hartzell · Thomas E. Jordan

Abstract Phosphorus (P) availability in estuaries may increase with increasing salinity because sulfate from sea salt supports production of sulfide in sediments, which combines with iron (Fe) making it less available to sequester P. Increased P availability with increased salinity may promote the generally observed switch from P limitation of primary production in freshwater ecosystems to nitrogen (N) limitation in coastal marine waters. To investigate this hypothesis, we analyzed pore water from sediment cores collected along the salinity gradients of four Chesapeake Bay estuaries (the Patuxent, Potomac, Choptank, and Bush Rivers) with watersheds differing in land cover and physiography. At salinities of 1–4 in each estuary, abrupt decreases in pore water Fe^{2+} concentrations coincided with increases in sulfate depletion and PO_4^{3-} concentrations. Peaks in water column PO_4^{3-} concentrations also occur at about the same position along the salinity gradient of each estuary. Increases in pore water PO_4^{3-} concentration with increasing salinity led to distinct shifts in molar $NH_4^+:PO_4^{3-}$ ratios from >16 (the Redfield ratio characteristic of phytoplankton N:P) in the

freshwater cores to <16 in the cores with salinities >1 to 4, suggesting that release of PO_4^{3-} from Fe where sediments are first deposited in sulfate-rich waters could promote the commonly observed switch from P limitation in freshwater to N limitation in mesohaline waters. Finding this pattern at similar salinities in four estuaries with such different watersheds suggests that it may be a fundamental characteristic of estuaries generally.

Keywords Phosphorus · Salinity · Pore water · Iron · Estuaries · Nitrogen

Introduction

Eutrophication of estuarine and coastal waters is a major environmental problem throughout the world and a challenge to our scientific understanding (Cloern 2001; Nixon 1995). Eutrophication is mainly driven by large-scale anthropogenic alterations of the cycles of N and P (Carpenter et al. 1998). It can cause depletion of dissolved oxygen, demise of submerged aquatic vegetation, and blooms of harmful algae, ultimately leading to losses of critical habitats and collapses of fisheries (Cloern 2001). The earliest studies of eutrophication focused on lakes but the scientific paradigms for freshwater later proved inadequate for marine systems (Cloern 2001). In freshwater, P usually limits primary production. P supply may also set the long-term limit on oceanic

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production (Tyrrell 1999). However, N usually limits production in coastal seawaters (e.g., Howarth and Marino 2006). In estuaries, where freshwater and seawater mix, spatial and temporal changes in the relative availabilities of N and P cause shifts in nutrient limitation (e.g., Doering et al. 1995; Fisher et al. 1999), which present difficulties for prioritizing nutrient management (Conley 2000).

One key reason for the nutrient limitation switch may be that iron (Fe) is less available to sequester phosphate (PO_4^{3-}) in saline sediments than in freshwater sediments, making P more bioavailable in coastal marine environments relative to N. In both freshwater and saltwater sediments, PO_4^{3-} bound to particulate Fe(III) oxides can be released to solution when the Fe(III) is reduced to Fe(II) after deposition in anoxic sediments. In freshwater sediment, Fe(II) can block PO_4^{3-} from diffusing to the overlying water column by combining with PO_4^{3-} to form vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) or other particulate ferrous compounds. Additionally, dissolved Fe(II) and PO_4^{3-} may both diffuse upward toward the overlying water and, if the surface freshwater sediments are aerobic, the Fe(II) may become oxidized to Fe(III) and precipitate with PO_4^{3-} (Carignan and Flett 1981; Chambers and Odum 1990; Cornwell 1987). However, in sulfate-rich saltwater sediments, Fe(II) instead precipitates with sulfide formed by sulfate (SO_4^{2-}) reduction in the anoxic layers of the sediment (Cornwell 1987; Gächter and Müller 2003; Postma 1982; Roden and Edmonds 1997). Precipitation of iron sulfides prevents Fe(II) from either precipitating with PO_4^{3-} in the anaerobic sediments or diffusing to aerobic layers where it could re-oxidize and bind PO_4^{3-} (Jensen et al. 1995). Caraco et al. (1989, 1990) suggested that the precipitation of iron sulfides can account for differences among fresh, brackish, and salt-water sediments in their capacities to retain PO_4^{3-} generated by decomposition of organic P. They also proposed that the greater retention of P in freshwater sediments compared to saltwater sediments could account for the general paradigm of P limitation in freshwater and N limitation in saltwater (Caraco et al. 1989, 1990).

We hypothesize that the increase in availability of P relative to N in estuaries is further promoted by salinity-enhanced conversion of terrigenous inorganic particulate P to dissolved PO_4^{3-}. More than 90% of the P carried by rivers to estuaries is associated with suspended solids and much of that is bound to Fe(III) (Föllmi 1996). When terrigenous Fe(III) bound P is deposited in estuaries, its release as dissolved PO_4^{3-} is stimulated by sulfide, as described above. Compared to release of PO_4^{3-} from organic P, release from inorganic P may be more important in shifting the relative availability of P and N along estuarine salinity gradients. Decomposition of organic matter releases N as well as P and therefore the effect of mineralization on the relative abundance of N and P depends on the N:P ratio of the organic matter. In contrast, release of PO_4^{3-} from inorganic P is not accompanied by release of N. Release of PO_4^{3-} from inorganic P in terrigenous sediments apparently increases PO_4^{3-} concentration in the water column of the upper Rhode River estuary (Jordan et al. 1991) and the upper Patuxent River estuary (Hartzell et al. 2010; Jordan et al. 2008).

Here we examine the generality of this phenomenon by comparing concentrations of dissolved PO_4^{3-}, NH_4^+, Fe^{2+}, and other solutes in sediment pore water along salinity gradients in four Chesapeake Bay estuaries representing watersheds that differ greatly in land cover and physiography. These estuaries include the Patuxent River estuary where we have previously examined interactions of Fe and P (Hartzell et al. 2010; Jordan et al. 2008) as well as the Potomac, Choptank, and Bush River estuaries. Despite the hypothesized importance of salinity, few studies have examined changes in P biogeochemistry along salinity gradients spanning fresh to brackish water.

Study sites

All four rivers are estuaries of the Chesapeake Bay (Fig. 1), and have mean tidal fluctuations of <1 m. The watersheds of the estuaries differ in land cover, with the Choptank watershed dominated by agriculture, the Potomac watershed dominated by forest, and the Patuxent and Bush watersheds more urbanized than the other two (Table 1). The Choptank watershed is entirely in the Coastal Plain physiographic province and the Patuxent watershed is predominantly in the Coastal Plain, while the Bush watershed is mainly in the Piedmont and the Potomac watershed is mainly in the Appalachian province (Table 1).

Fig. 1 Map of the
Chesapeake Bay showing
the four estuaries. Mean
pore water salinity values
are shown in parentheses at
the numbered sampling
sites
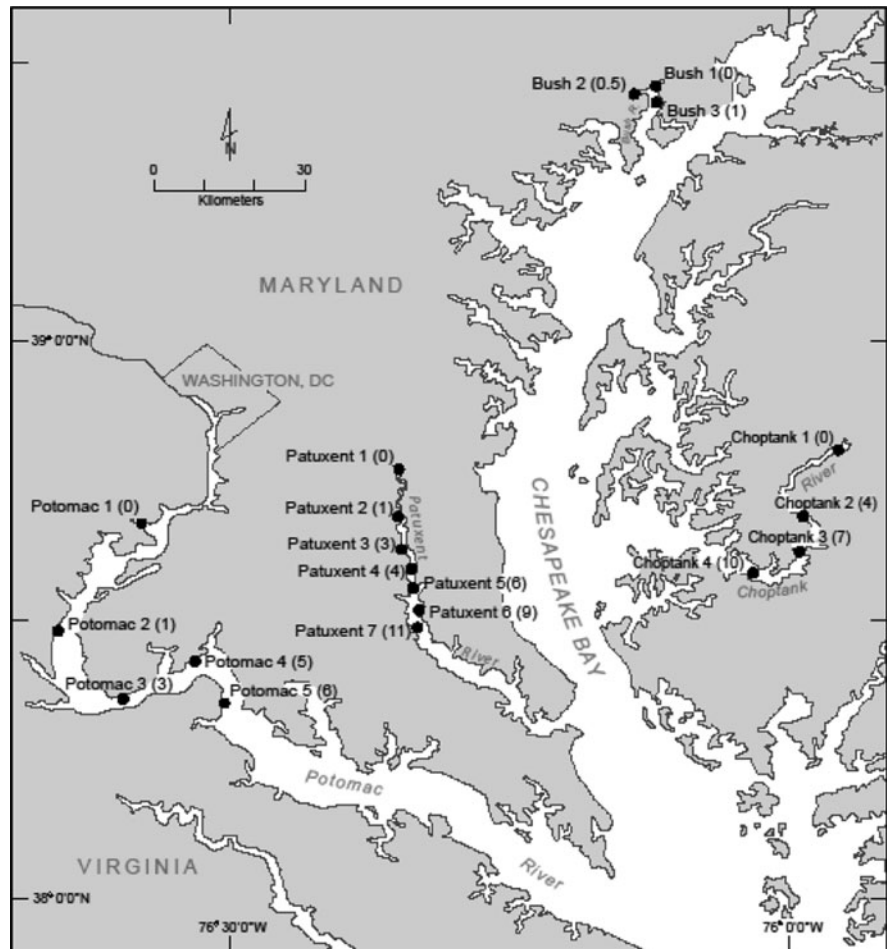
Methods

Sediment core collection and processing

We used a hand-operated piston-corer to collect 1 m long sediment cores in water that ranged from 1 to 7 m deep at seven different locations in the Patuxent, five in the Potomac, four in the Choptank, and three in the Bush River (Fig. 1). In the Patuxent River, we collected three replicate cores at site 2, five replicate cores at site 6, and two replicate cores at site 7. The sediment cores were collected during a range of months that spanned from April to November during 2005 and 2006. When replicate data are available, we report mean concentrations and standard deviation of the mean. The coring locations spanned pore water salinity gradients of 0–11 in the Patuxent, 0–6 in the Potomac, 0–10 in the Choptank, and 0–1 in the Bush River (practical salinity ratio similar to parts per

thousand). In the Bush River, the range of salinities that could be sampled was limited by proximity to the freshwater head of the Chesapeake Bay and by military restrictions on access.

The sediments were extruded vertically from the top of the core into a nitrogen glove bag using a hydraulic jack positioned at the bottom of the core. Two-centimeter thick samples were collected from the core at 10 cm intervals (i.e., from 9–11, 19–21, 29–31 cm, etc.). We refer to the samples by their mid-section depth (i.e., the 9–11 cm sample is referred to as 10 cm, 19–21 cm as 20 cm, etc.). The sediment samples were loaded into 50 ml polyethylene centrifuge tubes that were capped while still in the glove bags. The sediments were then centrifuged at 1,800g for 30 min and the supernatant pore water was removed with a syringe and filtered through 0.45 μm nitrocellulose Millipore syringe filters.

Table 1 Characteristics of the watersheds of the four estuaries: watershed area in 10^3 km^2; percentages of developed land, agricultural land, forested land, and wetlands; human population density per km^2; and % physiographic province

Estuary	Area 10^3 km^2	% Urban	% Agric.	% Forested	% Wetland	Pop. km^{-2}	Physiogr. provinces
Patuxent	2.3	17	36	42	4	264.3	C = 72%
							P = 28%
Potomac	36.5	11	31	57	1	145.2	A = 68%
							P = 20%
							C = 11%
Choptank	1.7	3	65	26	6	41.1	C = 100%
Bush	0.3	22	38	32	7	150.3	P = 70%
							C = 30%

The land cover percentages are NLCD2001 land cover data (Homer et al. 2004) summarized for the coastal tributary catchments defined in the NHDPlus data set (National Hydrography Dataset Plus (NHDPlus) 2009). Physiographic provinces were summarized by intersecting a USGS map of Chesapeake Bay physiographic provinces (Langland et al. 1995) with subbasin outlines from the NHDPlus for the Choptank, Potomac, and Patuxent (National Hydrography Dataset Plus (NHDPlus) 2009) and a Maryland state subbasin outline for the Bush River (Maryland Department of Natural Resources 1998). Population densities were calculated by the Chesapeake Bay Program Office using data collected by the U.S. Census Bureau in 2000

A Appalachian, *P* Piedmont, *C* Coastal Plain

Analytical methods

Concentrations of soluble reactive phosphorus in the filtered pore water were quantified using an ascorbic acid, molybdate colorimetric method (Eaton et al. 1995). We refer to this molybdate-reactive P as PO_4^{3-} in this paper. Color development for pore water PO_4^{3-} was carried out in the vial used for sample storage to ensure that any PO_4^{3-} that precipitated with Fe(III) during storage would be redissolved during the analysis rather than be lost on the walls of the storage vials. The detection limit (DL) for PO_4^{3-} was about 0.3 μmol l^{-1}. Total Fe dissolved in the pore water was measured using a Perkin Elmer Optima model 3000 Inductively Coupled Plasma, Optical Emission Spectrometer (DL = 1 μmol l^{-1}). Dissolved NH_4^+ was analyzed with an Astoria Pacific automated analyzer (Method A303-S02, DL = 0.7 μmol l^{-1}). Pore water Cl$^-$ and SO_4^{2-} concentrations were measured with a Dionex model 4000 ion chromatograph (DL = 0.6 μmol l^{-1}). Pore water salinity was calculated from Cl$^-$ concentrations. Since practical salinity is a ratio, we report salinity without units, but the measurements are approximately equal to parts per thousand. We estimated SO_4^{2-} depletion by subtracting the measured SO_4^{2-} concentration from that predicted from mixing freshwater with ocean water (0.86 mmol l^{-1} Cl$^-$, 0.16 mmol l^{-1} SO_4^{2-}) to produce the observed Cl$^-$ concentrations. Pore water pH was measured with a Fisher Scientific Accumet model 910 pH meter.

Results

Pore water solute trends with salinity and depth in the sediment

Pore water Fe^{2+} declined and PO_4^{3-} concentrations increased as salinity increased along the salinity gradient of each of the four estuaries, even in the Bush River where the salinity gradient was very slight (Fig. 2). In each estuary, an abrupt drop in Fe^{2+} with increasing salinity coincided with an abrupt increase in PO_4^{3-}. NH_4^+ concentrations generally declined with increasing salinity but trends were not as strong or consistent as the salinity-related trends of Fe^{2+} and PO_4^{3-}. Pore water NH_4^+ concentrations increased with depth in the sediments of most of the sites, while PO_4^{3-} concentrations increased with depth only in some of the more saline sites (Fig. 2). There was no clear trend in pore water Fe^{2+} concentrations with depth (Fig. 2). Averaging concentrations across all depths, mean pore water Fe concentrations declined by 88–100% with increasing salinity, while mean PO_4^{3-} concentrations increased by a similar proportion, 90–97%. By comparison, mean NH_4^+ concentrations declined along the salinity
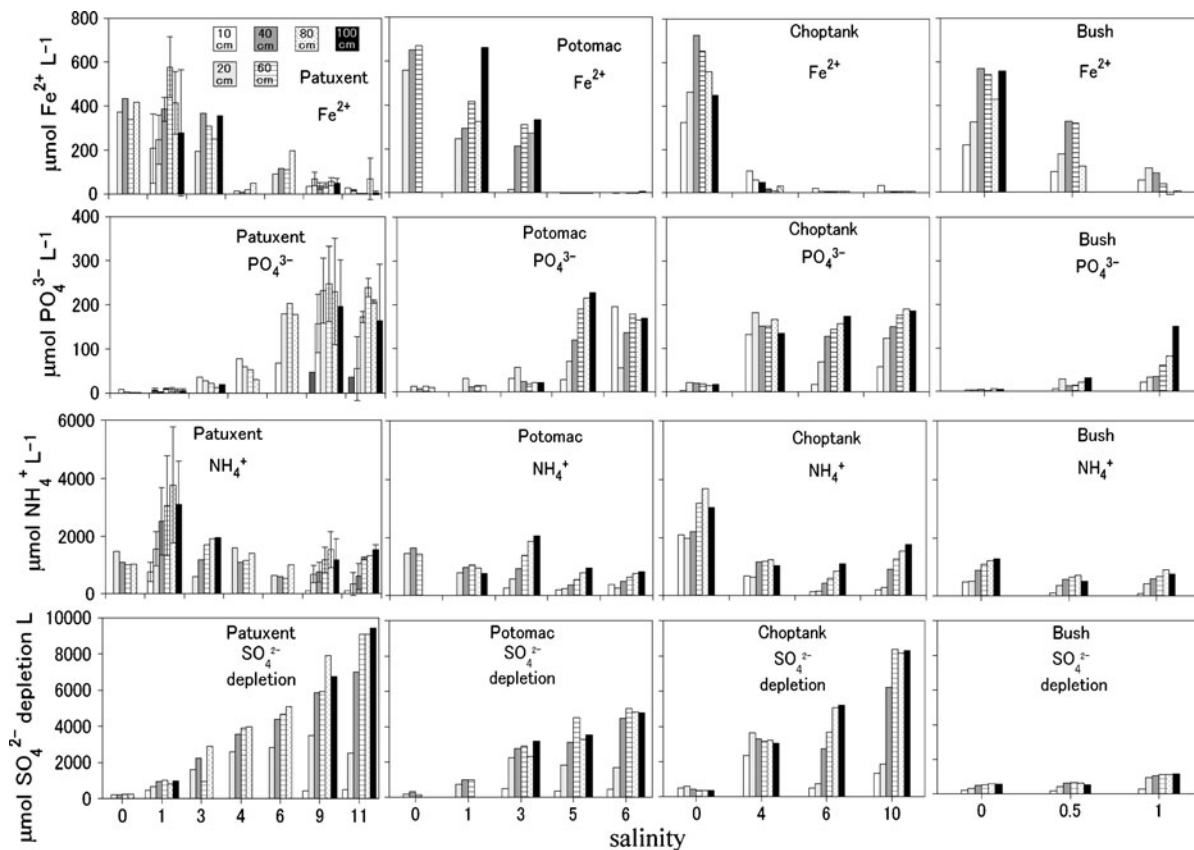
Fig. 2 Pore water Fe^{2+}, PO_4^{3-}, and NH_4^+ concentrations and SO_4^{2-} depletion in µmol l^{-1} at different depths in the sediments. *Error bars* depict standard deviation when replicate cores were available

gradient by 43–69%. In the Potomac and the Patuxent estuaries the highest concentrations of NH_4^+ did not occur in the pore waters of the freshest sites (Fig. 2). Trends with salinity were clear despite the variability among the replicate cores (Fig. 2), which was much higher than the <5% variance among analytical replicates.

Pore water sulfate (SO_4^{2-}) concentrations increased with salinity, reflecting the contribution from sea salts. However, the SO_4^{2-} increase was not as much as would be expected from the mixing of fresh and saline water because some of the SO_4^{2-} was reduced to sulfide. SO_4^{2-} depletion increased with salinity and usually with depth in the sediments, with SO_4^{2-} becoming almost completely consumed at the deepest depths (Fig. 2). Pore water pH increased with salinity in each of the four estuaries with pH values ranging from 6.7 to 7.0 in the freshwater sites to 8.0–8.7 in the most saline sites

(not shown). We found no trends in pore water pH with depth in the sediments.

Salinity related trends in pore water $Fe^{2+}:PO_4^{3-}$ and $NH_4^+:PO_4^{3-}$ ratios

The contrasting salinity related trends of pore water PO_4^{3-} and Fe^{2+} concentrations led to distinct shifts in the molar ratios of $Fe^{2+}:PO_4^{3-}$ in the pore water along the salinity gradients of all four estuaries, with $Fe^{2+}:PO_4^{3-}$ ratios consistently higher in the freshwater sediments than in the more saline sediments (Fig. 3). There were no trends in pore water $Fe^{2+}:PO_4^{3-}$ ratios with depth in the sediments (not shown).

The contrasting trends of NH_4^+ and PO_4^{3-} led to distinct declines in molar ratios of $NH_4^+:PO_4^{3-}$ in pore water with increased salinity in all four estuaries (Fig. 4). Pore water $NH_4^+:PO_4^{3-}$ ratios were >16
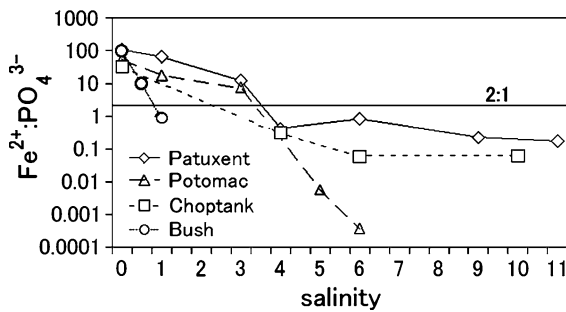
Fig. 3 Mean pore water $Fe^{2+}:PO_4^{3-}$ ratios along the salinity gradients of the four estuaries. Ratios are mean values of all depths for the entire length of the core(s) collected at a site
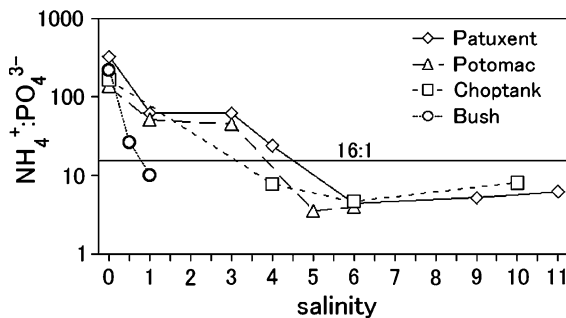

Fig. 4 Mean pore water $NH_4^+:PO_4^{3-}$ ratios along the salinity gradients of the four estuaries. Ratios are mean values of all depths for the entire length of the core(s) collected at a site

(the Redfield ratio characteristic of phytoplankton N:P) at most sites with salinities <4, while ratios were <16 at most sites with salinities >4. There were no clear trends in pore water $NH_4^+:PO_4^{3-}$ ratios with depth in the sediments (not shown).

Discussion

Controls on pore water Fe^{2+} and PO_4^{3-} concentrations along the salinity gradients

The pattern of declining pore water Fe^{2+} concentrations and increasing pore water PO_4^{3-} concentrations with increasing salinity in all four estuaries indicates that in more saline sediments less soluble Fe^{2+} is available to potentially precipitate with PO_4^{3-} after its re-oxidation in the benthic surface layer. Molar ratios of $Fe^{2+}:PO_4^{3-}$ in pore water were >2 in the freshwater regions and <2 at salinities >1 to 4 (Fig. 3). A ratio of at least 2 is required to block all

the PO_4^{3-} from diffusing to the water column by precipitation with Fe(III) in surficial aerobic sediments (Blomqvist et al. 2004; Gunnars et al. 2002), while a ratio of at least 1.5 is required to sequester all the PO_4^{3-} by precipitation with Fe(II) in anoxic sediments (Gächter and Müller 2003). Evidently, there is insufficient Fe^{2+} to prevent efflux of some pore water PO_4^{3-} from sediments with salinities >1 to 4. Other studies have suggested that sulfide produced from sulfate reduction precipitates Fe^{2+} in sediments thereby increasing the mobility of PO_4^{3-} (e.g., Blomqvist et al. 2004; Caraco et al. 1989). In our study, we found that at salinities of 1–4, pore water Fe^{2+} concentration drops coincided with locations where SO_4^{2-} became depleted by 1,000–2,000 $\mu mol\ l^{-1}$ relative to the concentration expected from mixing fresh and saline water (Fig. 2).

Controls on pore water NH_4^+ concentrations along the salinity gradients

In all four estuaries there was a general pattern of decline in pore water NH_4^+ concentrations with increased salinity, which reflects a similar gradient in dissolved inorganic nitrogen (DIN, the sum of nitrate, nitrite, and NH_4^+) in the water column caused by DIN (primarily nitrate) inputs from the watershed. Water column DIN assimilated by phytoplankton or other biota and later re-mineralized in the sediment accumulates in pore water as NH_4^+. Thus, declining NH_4^+ concentrations in the water column or pore waters with increased salinity can often be related to distance from watershed N sources (Boynton and Kemp 2008). However, the trend in pore water NH_4^+ did not perfectly mirror that of the water column DIN. In the Patuxent and Potomac estuaries the highest pore water NH_4^+ did not occur at the least saline site (Fig. 2).

Other factors besides N loading from the watershed can also affect NH_4^+ patterns with salinity. For example, NH_4^+ that is loosely sorbed to sediment particles can be released into pore water solution because of displacement with cations or ion pairing anions in saltwater (Gardner et al. 1991; Seitzinger et al. 1991). Thus in some estuaries pore water NH_4^+ concentrations can increase when exposed to increased salinity (Andrieux-Loyer et al. 2008; Hopkinson et al. 1999). However, in our study sites, salinity-driven desorption of NH_4^+ apparently had

less influence than did the proximity to watershed N sources.

Which nutrient exerts greater control over the $NH_4^+:PO_4^{3-}$ ratio switch?

Trends in both the PO_4^{3-} and NH_4^+ pore water concentrations with increased salinity caused a switch in molar $NH_4^+:PO_4^{3-}$ ratios from >16 to <16 at salinities of 1–4 in all four estuaries (Fig. 4). However, the $NH_4^+:PO_4^{3-}$ ratio was more dependent on changes in PO_4^{3-} concentrations than on changes in NH_4^+ concentrations. In all four estuaries, if NH_4^+ concentrations had remained constant at the freshwater values, and only PO_4^{3-} concentrations changed along the salinity gradient, $NH_4^+:PO_4^{3-}$ ratios would have dropped to ≤16 by a salinity of about 6 (Fig. 5a). On the other hand, if PO_4^{3-} concentrations remained constant at the freshwater values, and only NH_4^+ concentrations declined along the salinity gradient, $NH_4^+:PO_4^{3-}$ ratios would have remained >16 at all salinities in all four estuaries (Fig. 5b). Thus, it appears that salinity-induced changes in pore water PO_4^{3-} concentrations alone could alter the pore water $NH_4^+:PO_4^{3-}$ ratios enough to shift across the Redfield ratio along the salinity gradients.
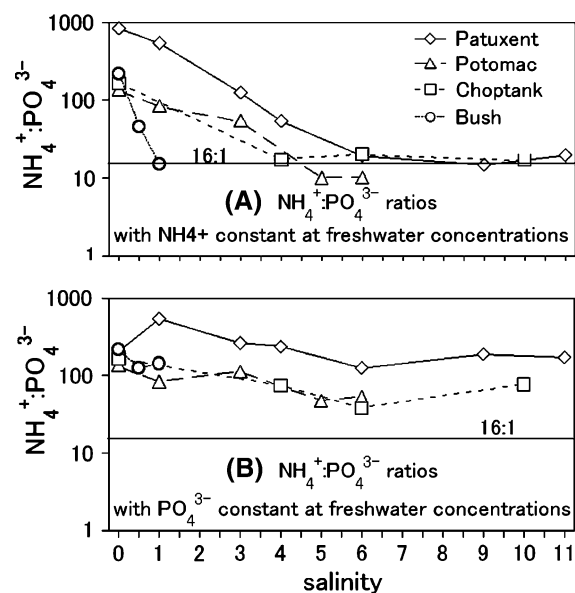

Fig. 5 Mean pore water $NH_4^+:PO_4^{3-}$ ratios along the salinity gradients of the four estuaries if: **a** PO_4^{3-} remained constant at freshwater concentrations and **b** NH_4^+ remained constant at freshwater concentrations

We found few other published reports of pore water $NH_4^+:PO_4^{3-}$ ratios along salinity gradients from tidal fresh to mesohaline waters. One exception is a study of intertidal marsh sediments which reported pore water $NH_4^+:PO_4^{3-}$ ratios >16 in fresh water sediments and <16 at water column salinities of 0.44 and higher (Sundareshwar and Morris 1999), which is a lower salinity than the lowest salinity where we observed the $NH_4^+:PO_4^{3-}$ ratio switch (i.e., 0.5–1 for the Bush River, Fig. 4). A $NH_4^+:PO_4^{3-}$ ratio switch at a lower salinity in intertidal marshes may reflect N uptake by emergent marsh plants, which have high N demands (Crain 2007). Two reports of pore water $NH_4^+:PO_4^{3-}$ ratio changes with salinity in subtidal sediments were complicated by large seasonal or tidal fluctuations in water column and pore water salinity, thus the salinity level where the 16:1 switch may occur was unclear (Andrieux-Loyer et al. 2008; Hopkinson et al. 1999).

Effects on N and P availability in the water column

The elevated concentration of PO_4^{3-} we found in the saline sediments (Fig. 2) suggests a stronger potential for PO_4^{3-} efflux from saline sediments than from freshwater sediments. However, efflux of solutes may be strongly influenced by the concentration gradients in the top few cm of the sediment, which we did not sample. In any case, elevated PO_4^{3-} concentrations in the pore water do not necessarily indicate elevated PO_4^{3-} efflux from the sediments. Release of PO_4^{3-} from the sediments may be blocked by precipitation with oxidized Fe in the surface oxidized layer of the sediments (e.g., Blomqvist et al. 2004). However, such precipitation would probably be somewhat limited in the saline sediments we studied because the molar ratios of $Fe^{2+}:PO_4^{3-}$ in pore water were <1 at salinities >4 (Fig. 3) while a ratio of at least 2 is required for precipitation with Fe(III) to block all the PO_4^{3-} from diffusing to the water column (Blomqvist et al. 2004; Gunnars et al. 2002).

Direct measurements of PO_4^{3-} efflux from estuarine sediments are consistent with our hypothesis that P–Fe–S interactions promote release of PO_4^{3-} from the sediments at salinities >1 to 4. Comparing PO_4^{3-} efflux from 48 estuarine sites outside of Chesapeake Bay, Boynton and Kemp (2008) found

the lowest rates in tidal freshwaters (salinity 0–0.5), averaging about 4 μmol P m^{-2} h^{-1}; while rates were higher at salinities of 0.5–5, averaging about 12 μmol P m^{-2} h^{-1}; and highest at salinities of 5–10, averaging about 52 μmol P m^{-2} h^{-1}. Reviewing efflux measurements from 300 sites in 27 Chesapeake tributary estuaries and along the main axis of Chesapeake Bay, Boynton and Bailey (2008) found a similar relationship between salinity and PO$_4$$^{3-}$ efflux, with rates averaging about 6 μmol P m^{-2} h^{-1} at 0–0.5 salinity, 12 μmol P m^{-2} h^{-1} at 0.5–5 salinity, and 20 μmol P m^{-2} h^{-1} at 5–10 salinity.

PO$_4$$^{3-}$ efflux from Potomac River sediments differed somewhat from the general pattern due to exceptionally high PO$_4$$^{3-}$ efflux rates in low salinities, causing average rates to peak at 20 μmol P m^{-2} h^{-1} at salinities of 0.5–5 (Boynton and Bailey 2008). This may reflect episodic increases in surface water pH to levels >9.5 driven by phytoplankton blooms (Boynton and Bailey 2008). Seitzinger (1991) demonstrated the enhancement of PO$_4$$^{3-}$ efflux from tidal freshwater Potomac sediments due to increase in pH above 9.5. Similar pH effects have been shown in eutrophic lakes and attributed to ion exchange of hydroxide for PO$_4$$^{3-}$ on metal oxide surfaces (Jensen and Andersen 1992; Xie et al. 2003). We did not observe elevated PO$_4$$^{3-}$ concentrations in Potomac sediments at salinities of 0–3 (Fig. 2) but pH was ≤8.1 in all of the Potomac sediments we sampled. Nevertheless, it is clear that high pH can stimulate PO$_4$$^{3-}$ effluxes independent of Fe–S interactions.

P–Fe–S interactions may account for observations that PO$_4$$^{3-}$ effluxes from sediments in the Chesapeake Bay and other estuaries and coastal areas are generally highest at salinities of 5–10 (Boynton and Kemp 2008, Boynton and Bailey 2008). These effects might also explain why PO$_4$$^{3-}$ concentrations in the water column of the Chesapeake Bay are consistently higher at salinities of 3–4 than predicted by water quality models that do not account for P–Fe–S interactions (Cerco and Cole 1993). Similarly, year-round peaks in water column PO$_4$$^{3-}$ concentrations at salinities of 1–4 in all four estuaries (Fig. 6) suggest that PO$_4$$^{3-}$ released from sediments at these salinities, elevates PO$_4$$^{3-}$ concentration in the water column. All of these observations support the hypothesis that P–Fe–S interactions are promoting a release of PO$_4$$^{3-}$ from the sediments at salinities of
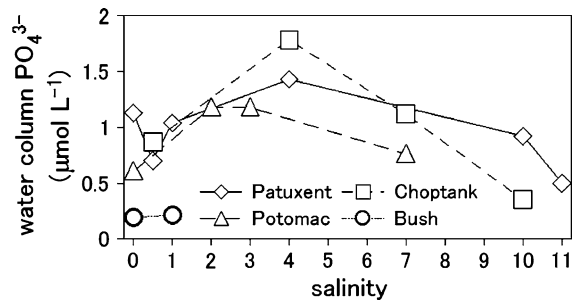

Fig. 6 Mean water column PO$_4$$^{3-}$ concentrations along the salinity gradients of the four estuaries. Data are from the Chesapeake Bay Program for samples collected throughout the year from 1996 to 2006. Samples were collected once per month during the colder late fall and winter months and twice per month in the warmer months

1–4, and that this release can alter the relative bioavailability of N and P.

Potential nutrient limitation depends on the relative availability of N and P to phytoplankton, usually defined as relative concentrations of DIN and PO$_4$$^{3-}$. In the water columns of the estuaries we studied, DIN:PO$_4$$^{3-}$ varies spatially and seasonally (Chesapeake Bay Program 1984–present). Our estuaries, like most temperate estuaries, receive the highest watershed inputs of both freshwater and DIN (primarily as nitrate (NO$_3$$^{-}$) in the spring). Higher inputs of DIN can contribute to P limitation and contribute to observed seasonal changes in potential nutrient limitation. In estuaries, NO$_3$$^{-}$-enriched water from the watershed is diluted by NO$_3$$^{-}$-poor seawater producing a gradient of declining NO$_3$$^{-}$ (and thus declining DIN) concentration with increasing salinity. The decline in NO$_3$$^{-}$ in the estuary is enhanced due to denitrification and uptake by phytoplankton and other biota. In anoxic sediments, such as we studied, NO$_3$$^{-}$ is an electron acceptor in denitrification and is completely consumed within a few cm of the sediment surface (e.g., Jordan et al. 2008). At our study sites the spring NO$_3$$^{-}$ loads are high enough that ratios remain >16 at most locations, although yearly averages of water column DIN:PO$_4$$^{3-}$ decline along the salinity gradient (Fig. 7a). However, in the summer months, the dilution and consumption of NO$_3$$^{-}$ and, potentially, the release of PO$_4$$^{3-}$ from sediments cause water column DIN:PO$_4$$^{3-}$ ratios to decline below 16 at salinities of 0.5–7 in all four of our subestuaries (Chesapeake Bay Program 1984–present) (Fig. 7b).
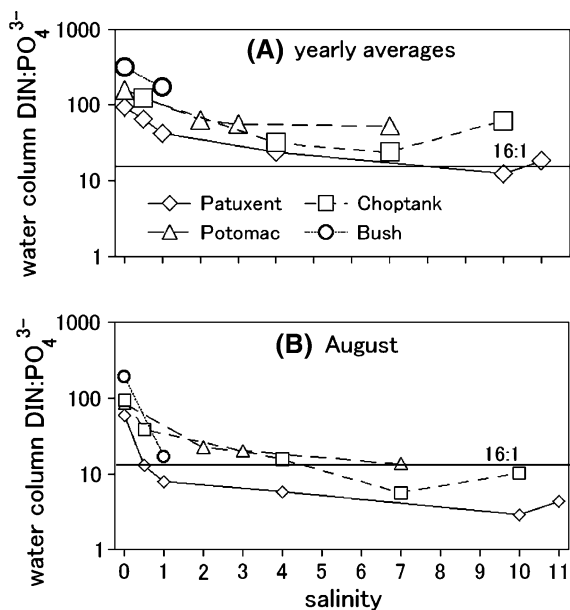
Fig. 7 Mean water column $DIN:PO_4^{3-}$ ratios along the salinity gradients of the four estuaries. Data are from the Chesapeake Bay Program for samples collected from 1996 to 2006 and **a** throughout the year and **b** during the month of August

The similarity in the location of the 16:1 ratio switch in the pore water and the water column suggests that water column nutrient concentrations are influenced by sediment biogeochemical processes, especially in the summer, when DIN loads and freshwater discharges decline (Figs. 4, 7b). At all times of the year PO_4^{3-} and NH_4^+ concentrations are higher in the pore water than in the overlying water column (e.g. Figs. 2, 6), suggesting flux out of the sediments. When NH_4^+ enters the water column it may be oxidized to NO_3^- by nitrifying bacteria. NO_3^- concentrations are higher in the water column than in the sediment, indicating flux into the sediment, but DIN concentrations indicate an overall net flux of DIN out of the sediment. To completely assess the relative importance of sediment–water column exchanges in controlling concentrations in the water column we would need to compare rates of those exchanges with rates of input from the watershed and surface water mixing along the estuary. This is beyond the scope of our study, but the year-round peaks in water column PO_4^{3-} concentrations at salinities of 1–4 in all four estuaries (Fig. 6) suggest that PO_4^{3-} released from sediments

at these salinities elevates PO_4^{3-} concentration in the water column. This hypothesis is also supported by reports that sediment PO_4^{3-} flux is consistently elevated at salinities of 5–10 in the Chesapeake Bay (Boynton and Bailey 2008) and other estuaries and coastal areas (Boynton and Kemp 2008).

In contrast to the seasonal trends of nutrients in the surface waters, we found no correlation in pore water concentrations of NH_4^+, PO_4^{3-}, and Fe^{2+} and the month the core was collected from April to November. Perhaps the time required for diffusion between sediments and pore water dampens the seasonal fluctuations in pore water, especially at the lowest depths we sampled. Thus, using mean values of pore water salinities and solutes to depths of up to 100 cm may have allowed us to locate the $NH_4^+:PO_4^{3-}$ ratio switch along the salinity gradient without interference from seasonal variability.

Significance for nutrient limitation

While we did not measure nutrient limitation per se, we have shown that, in our four estuaries, $DIN:PO_4^{3-}$ drops below 16:1 in the pore water when pore water Fe^{2+} concentration drops at salinities >1 to 4, coinciding with year-round peaks in water column PO_4^{3-} and seasonal shifts in water column $DIN:PO_4^{3-}$ ratios. The shift below the 16:1 Redfield ratio of phytoplankton N and P requirements suggests that the potentially limiting nutrient changes from P to N as salinity increases above 4. Our data suggest that the drop in Fe^{2+} and the increase in PO_4^{3-} in the pore water play an important role in the change in the relative availability of N and P.

Other factors could also contribute to the general pattern of P limitation in freshwater and N limitation in coastal saltwater. Most notably, N fixation by planktonic cyanobacteria can alleviate N limitation in freshwaters (e.g., Schindler 1977) but usually not in coastal marine waters where several factors reduce cyanobacteria populations or N fixation ability at salinities >10 to 12 (Howarth and Marino 2006). In many ecosystems, the energy demand of N fixation may restrict its ability to alleviate N limitation. A frequently-cited model of nutrient limitation in the ocean starts from the premise that the energy requirements of N fixation prevent it from alleviating short-term N limitation (Tyrrell 1999). Along the estuarine salinity gradients we studied, the surface

waters are likely to be too turbid and too rapidly flushed to support planktonic N fixation.

Still other factors have been suggested to account for differences in nutrient limitation in freshwater versus coastal marine water. For example, it has been proposed that denitrification might have a greater effect of removing DIN in estuaries or coastal waters than in freshwater. However, evidence for such a systematic difference in denitrification rates is lacking, and it could be argued that denitrification might deplete DIN to a greater extent in lakes, which generally have longer water residence times than do estuaries (Howarth and Marino 2006). Nevertheless, denitrification in coastal waters might partly account for the general tendency for DIN concentrations to decline as salinity increases in estuaries, which contributes to the drop in $DIN:PO_4^{3-}$, as we discussed earlier. It has also been suggested that sewage discharges from urban areas adjacent to estuaries add PO_4^{3-} in greater amounts than DIN, thus alleviating P limitation (Howarth and Marino 2006). However, sewage outfalls do not account for the peaks in surface water PO_4^{3-} concentrations along the salinity gradients we studied (Fig. 6).

Unloading the iron conveyer belt

The peaks in surface water PO_4^{3-} concentrations along the salinity gradients (Fig. 6) probably reflect the release of inorganic Fe(III) bound PO_4^{3-} that was delivered to the estuary on particulate matter from the watershed. More than 90% of the P carried by rivers to estuaries is associated with suspended solids and much of that is bound to Fe(III) (Föllmi 1996). During transport through freshwater ecosystems, P tends to remain bound to Fe, but upon delivery to estuaries, the formation of Fe sulfides enhances PO_4^{3-} release to the water column. Thus, Fe flowing from land to sea acts as a conveyer belt carrying PO_4^{3-} through freshwater environments until it is unloaded in sulfate-rich saline waters (Jordan et al. 2008). Release of PO_4^{3-} from inorganic particulate matter is especially effective at changing the relative abundance of N and P because it is not accompanied by the release of DIN whereas the decomposition of organic matter releases both N and P. Based on analysis of P budgets, release of PO_4^{3-} from inorganic PP in terrigenous sediments appears to be the most important mechanism accounting for the

peak in PO_4^{3-} concentration in the upper Patuxent River estuary (Jordan et al. 2008) and in the nearby upper Rhode River estuary (Jordan et al. 1991). The portion of the salinity gradient where the Fe conveyer belt is being unloaded corresponds to the region where the PO_4^{3-} concentration peaks in the surface water.

Generality among estuaries

A salinity range of 1–4 is a remarkably consistent location for the 16:1 ratio switch among the four estuaries we studied, especially considering the differences in physiographic provinces and land use patterns of the watersheds (Table 1) that might affect the chemical form and concentration of P in the sediments and pore waters. For example, in the Chesapeake Bay watershed, the P concentration in particulate matter differs between the Piedmont and Coastal Plain physiographic provinces, with particulate matter from the Coastal Plain usually about four times as rich in P as that from the Piedmont (Jordan et al. 1997). Thus, the particulate matter entering the Choptank River and Patuxent River would likely be richer in P than that entering the Bush River. The Appalachian province includes carbonates in which P would be bound mainly to calcium rather than the Fe. Thus, while the Potomac watershed is predominantly non-carbonate, particulate P in Potomac River sediments might be less influenced by biogeochemical reactions with Fe than that in the other estuaries. Differences in the proportions of agricultural and urban land among the watersheds of our study estuaries could also affect the abundance of N and P because both of these land types are sources of N and P inputs to estuaries (Carpenter et al. 1998). Despite these differences, our estuaries showed similar shifts in the relative abundance of Fe^{2+}, PO_4^{3-}, and NH_4^+ in pore water and PO_4^{3-} and DIN in surface water along the salinity gradients. This suggests that changes in concentration ratios are governed mainly by the effect of salinity on SO_4^{2-} concentration and that the patterns of change along salinity gradients may be fundamental characteristics of estuaries with predominantly non-carbonate sediments.

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