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Effects of cyanobacterial-driven pH increases on sediment nutrient fluxes and coupled nitrification-denitrification in a shallow fresh water estuary

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Abstract

5 Summer cyanobacterial blooms caused an elevation in pH (9 to ~10.5) that lasted for weeks in the shallow and tidal-fresh region of the Sassafras River, a tributary of Chesapeake Bay (USA). Elevated pH promoted desorption of sedimentary inorganic phosphorus and facilitated conversion of ammonium (NH_4^+) to ammonia (NH_3). In this study, we investigated pH effects on exchangeable NH_4^+ desorption, nutrient pore water diffusion and flux rates of NH_4^+ , soluble reactive phosphorus (SRP), nitrate (NO_3^-), nitrification, denitrification, and oxygen consumption. pH elevation enhanced the desorption of exchangeable NH_4^+ because of NH_3 formation from both pore water and adsorbed NH_4^+ pools. Progressive penetration of high pH from the overlying water into sediment promoted the release of SRP and total ammonium (NH_4^+ and NH_3) into pore water. At elevated pH, high sediment-water effluxes of SRP and total ammonium were associated with reduction in nitrification, denitrification and oxygen consumption rates. Alkaline pH and the toxicity of NH_3 may inhibit nitrification in the thin aerobic zone, simultaneously constraining coupled nitrification-denitrification with limited NO_3^- supply and high pH penetration into the anaerobic zone. Geochemical feedbacks to pH elevation, such as enhancement of dissolved nutrient effluxes and reduction in N_2 loss via denitrification, may be responsible for the persistence of cyanobacterial blooms in shallow water ecosystems.

20 1 Introduction

Nutrient releases from sediment to the water column can support a substantial fraction of the primary production in shallow coastal and estuarine ecosystems (e.g. North Carolina estuaries, Fisher et al. 1982; Potomac River Estuary, Kemp and Boynton, 1984; Baltic Sea, Koop et al., 1990; Chesapeake Bay, Cowan and Boynton, 1996) Enhanced nitrogen and phosphorus fluxes may promote high levels of phytoplankton biomass (Kemp et al., 2005). Such phytoplankton blooms lead to the sustained accumulation of

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5 phytodetritus in sediment, fueling nutrient recycling through organic matter remineralization (Cowan and Boynton, 1996; Nixon et al., 1996). The consequences, such as decreased water clarity, depletion of bottom-water oxygen and the decomposition of phytodetritus, may enhance sediment respiration, decrease redox potential, limit nutrient uptake by benthic microalgae, and generally increase nutrient fluxes (Kemp et al., 2005).

10 In the deep, hypoxic region of the Chesapeake Bay and other estuaries, phosphorus flux is usually promoted by the dissolution of Fe-oxides and their conversion to iron sulfides; the increase in ammonium release from sediments tends to coincide with inhibition of nitrification by oxygen depletion and generation of reductants ($\text{HS}^-/\text{H}_2\text{S}$) in sediment, which consequently reduce denitrification (Kemp et al., 2005; Cornwell and Kana, 1999). In oxic shallow water ecosystems benthic nutrient releases are generally less redox influenced.

15 Persistent high pH in shallow water, driven by rapid utilization rates of inorganic carbon for photosynthesis during dense algal blooms (Hansen, 2002; Hinga, 2002), can influence benthic dynamics by progressive pH penetration from the overlying water into sediments (Bailey et al., 2006). When pH is above a critical threshold (9–9.2), inorganic phosphorus desorbs from iron oxides at mineral surfaces (Andersen, 1975; Eckert et al., 1997). Elevation of pore water pH (~9.8 in tidal-fresh region, Eckert et al., 1997) can release soluble reactive phosphorus (SRP) and support photosynthetic P demand during cyanobacterial blooms in lakes (Xie and Xie, 2003) and tidal fresh and oligohaline estuaries (Seitzinger, 1991; Andersen, 1975).

25 In contrast to pH-driven P cycling, the effects of pH on sediment N transformations and release are less well understood (Soetaert et al., 2007). During the decomposition of sediment organic matter, remineralized NH_4^+ may both adsorb onto sediment mineral surfaces and accumulate in pore water. Exchangeable NH_4^+ is weakly adsorbed at the negatively charged particle surfaces, buffering pore water NH_4^+ concentrations (Rosenfeld, 1979). In estuaries, fine grained sediment generally has a large pool of adsorbed NH_4^+ (Wang and Alva, 2000; Weston et al., 2010), with freshwater sediments having

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considerably more adsorbed ammonium relative to saline sediments (Seitzinger, 1991). Once alkaline pH results in the conversion of ammonium (NH_4^+) to dissolved ammonia (NH_3), formation of non-ionized NH_3 may decrease NH_4^+ cation adsorption on sediments and potentially alter the balance between pore water and exchangeable NH_4^+ .

Remineralized N can be assimilated by plants and bacteria or diffuse/ advect from sediment into the overlying water. Part of the NH_4^+ can be oxidized sequentially to $\text{NO}_2^-/ \text{NO}_3^-$ then reduced to N_2 through coupled nitrification-denitrification (Cornwell and Kana, 1999). However, shifts in the $\text{NH}_4^+ \text{-NH}_3$ equilibrium associated with high pH events may change rates of pore water diffusion, nitrification and denitrification. In the tidal-fresh and oligohaline parts of the Potomac River (Chesapeake Bay, USA), Seitzinger (1987) observed both increased SRP and NH_4^+ fluxes with pH elevation. Experimental NH_4^+ flux rates increased from <10 to over $100 \mu\text{mol m}^{-2} \text{h}^{-1}$ when pH was raised from 8 to 10 in laboratory incubations (Seitzinger, 1987). During a algal bloom in the Potomac estuary, Bailey et al. (2006) observed a three-fold increase of NH_4^+ efflux when the bottom water pH rose from neutral to above 9. In soil studies, the combined influence of alkaline pH (>8) and NH_3 production can decrease the NH_4^+ soil inventory by NH_3 volatilization, and change the efficiency of nitrification and denitrification by inhibiting bacterial activity (Simek et al., 2002; Cuhel et al., 2010).

We hypothesize that increased sediment pH facilitates not only P desorption but also the conversion of NH_4^+ to NH_3 with consequent changes in sediment N cycling. In this study we examined the pH effects on exchangeable NH_4^+ desorption using the surface sediments. Impacts of high pH conditions on the sediment-water nutrient exchange were estimated with changes in flux rates of SRP, NH_4^+ , NO_3^- , O_2 , and coupled nitrification-denitrification using intact sediment cores. We also calculated the diffusive flux rates of pore water NH_4^+ , NH_3 and SRP to confirm direct flux measurements. Due to the tightly coupled nitrification-denitrification, we independently measured nitrification rates using an inhibitor (Caffrey and Miller, 1995) and potential nitrification rates using slurries (Henriksen et al., 1981).

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We experimentally addressed these questions using sediment cores in the Sassafras River, a shallow, tidal freshwater tributary of the Chesapeake Bay (USA). As in other parts of the Chesapeake Bay (Tango and Butler, 2008), summer cyanobacterial blooms have been observed frequently in the Sassafras River in recent decades. Relative to sea water, tidal fresh and oligohaline water have low pH buffering (Price et al., 2008), facilitating high pH from cyanobacterial photosynthetic carbon uptake. In the Sassafras River, high pH persisted in the range of 9 to 10.5 for several weeks during dense cyanobacterial blooms in the summers of 2007 and 2010. When such high pH is in contact with bottom sediment, pH penetration into sediment can impact nutrient biogeochemical processes (Bailey et al., 2006).

2 Materials and methods

2.1 Study site and collection of cores

We collected sediments with 7 cm inner diameter, 30 cm long acrylic cores at two sites in the upper Sassafras River. The Powerline site ($75^{\circ}49.712'$, $39^{\circ}22.646'$) was sampled on 18 June 2008 and Budds Landing ($75^{\circ}50.380'$, $39^{\circ}22.310'$) was sampled on 14 July 2009 (Table 1). Dissolved oxygen (DO), salinity, pH and temperature were measured with a YSI 600XLM multiparameter sensor. Vertical irradiance profiles were recorded by a 2π Li-Cor underwater PAR light sensor. Bottom water collected for sediment incubations was filtered to minimize water column autotrophic and microbial respiration and nutrient recycling. Samples were transported to Horn Point Laboratory within 4 hours. Sediment cores were gently bubbled overnight to equilibrate temperature, O_2 , and N_2-N in the overlying and near surface pore waters (Kana et al., 2006). The surface sediments from Budds Landing were homogenized for potential nitrification measurements.

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2.2 Experimental design

We incubated experimental cores (at least triplicates) at several pH levels to investigate pH effects on nutrient exchange at the sediment-water interface. Sediment-free blank cores were incubated identically at each pH level to correct for water column metabolism. Consistent with an absence of photosynthetically active radiation at the sediment surface at the time of collection, a dark temperature-controlled environmental chamber was used to maintain the sediments and replacement-water reservoir at in situ water temperatures of 25 °C for Powerline and 27 °C for Budds Landing, respectively. The filtered water was bubbled with air to maintain oxygen saturation, adjusted to experimental pH with 0.1 mol L⁻¹ NaOH, and continuously pumped through the sediment overlying water (~500 ml) at 10 ml min⁻¹.

For the Powerline experiments, the overlying water pH of 4 replicate sediment cores was increased stepwise from 7.8 ± 0.5 (control) to 9.2 ± 0.05 (pH 1), and 9.6 ± 0.03 (pH 2), with a 5 day equilibration at each elevated pH. An alternative approach was used with sediments from Budds Landing (Table 2). Nine cores were incubated at ambient pH for the initial fluxes, and then triplicate cores were subjected to pH manipulation for each treatment. After 7 days of exposure to higher pH levels, the pH in the overlying water was 7.4 ± 0.3 (control), 9.2 ± 0.05 (pH 1) and 9.5 ± 0.2 (pH 2). Within each sealed core, suspended magnetic stir bars circulated water gently to keep it mixed below the threshold of sediment resuspension.

For both sites, nutrients fluxes (SRP, NH₄⁺, and NO₃⁻), oxygen consumption (O₂) and coupled nitrification-denitrification (net N₂ flux) were measured on the 1st day of incubation of sediments and after the pH reached the target values. After the termination of flux incubations, the top 11 cm sediments at each pH treatment were sectioned to collect pore water nutrients and to measure sediment pH. Duplicate sediment cores from Budds landing were used to measure nitrification rates, and Br⁻ was added to control cores as tracer to estimate diffusion/advection coefficients (Martin and Banta, 1992). The remaining sediment cores were used to estimate the percent water.

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2.3 Flux rates cross the sediment-water interface

Flux rates were measured on the first day of the incubation and after each equilibration period. The pumping of treatment water was interrupted during flux incubations and briefly restarted to collect samples every 1–2 h with a total of 4 time-points. Solute samples were filtered through a 0.45 μm cellulose acetate syringe filter and frozen at -4°C . Dissolved O_2 and N_2 subsamples were preserved in 7 ml glass tubes by adding 10 μl of 50 % saturated HgCl_2 solution (Kana et al., 2006), and then stored under water at near-ambient temperature until analysis. To preserve total dissolved ammonium ($\sum\text{NH}_x = \text{NH}_4^+ + \text{NH}_3$) at higher pH levels, 2.5 μl of 0.1 mol L^{-1} sulfuric acid was added into the sample vials. Flux rates were calculated from a regression of the time-concentration data in sediment and water column blank cores.

2.4 Sediment pore-water chemistry

Samples for pH and pore water analysis were sectioned over the top ~ 10 cm into 50 ml centrifuge tubes in a nitrogen-filled glove bag to minimize oxidation artifacts (Bray et al., 1973). Vertical changes of pH were measured immediately with a flat surface pH electrode. Pore water was separated from the solid phase by centrifugation at 2000 G for 10 min. Supernatant solutions were filtered through a 0.45 μm 25 mm diameter cellulose acetate syringe filter and appropriately diluted for analysis of Br^- , Fe, SRP, NH_4^+ , and $\sum\text{NH}_x$. The total iron, mostly Fe^{2+} , was acidified for preservation (Gibb, 1979).

2.5 Nitrification potential and nitrification rates

The effect of pH on nitrification was estimated using sediments from Budds Land-ing. Measurements included slurry incubation for potential nitrification (Henriksen et al., 1981) and CH_3F inhibition of intact sediments (Caffrey and Miller, 1995). In O_2 -saturated Sassafra River water, pH was pre-adjusted to values ranging from 7 to 11

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using NaOH. The NH_4Cl concentration was set to 1.0 mM, with triplicates at each pH level. For potential nitrification, the top 2 cm of sediment were homogenized with 1 ml added separately into centrifuge tubes with different pH's. The suspension was gently shaken in darkness at 27 °C and subsamples for NO_3^- were taken at 0, 12, and 24 h to calculate rates of potential nitrification. Changes of NO_3^- in a sediment-free control were used as a background correction. Although this method homogenizes the redox profile and the NH_4^+ gradient of the sediment and disrupts the aggregation of aerobic/ anaerobic microbiota (Killham, 1994; Garcia-Ruiz et al., 1998), it makes testing pH effects over a large pH gradient relatively simple.

An alternative to slurries was direct flux measurements using CH_3F to inhibit nitrification (Caffrey and Miller, 1995). The CH_3F method was carried out immediately after the end of flux measurements. Saturated solutions of CH_3F were injected into the overlying water of each intact core to a final concentration of $\sim 100 \text{ mg L}^{-1}$. After 24 h of aerobic dark pre-incubation, ammonium flux rates were measured using our standard flux procedure. Increased flux rates of ammonium after CH_3F treatment were interpreted as the nitrification rate. Shortcomings in the CH_3F -inhibition method may include increased accumulation of pore water ammonium and non-specific inhibition of other N transformations such as ammonification (Capone et al., 2009).

2.6 Molecular diffusive flux rates

Diffusion coefficients in sediment were estimated from Br^- penetration profile (Martin and Banta, 1992). Bromide (NaBr) was added as a tracer into the overlying water to a concentration of $\sim 6 \text{ mM}$. Pore water Br^- was sampled after 24 h to estimate a diffusion coefficient (D_{Br}), which was corrected for temperature and sediment porosity; the measure D_{Br} was compared to the theoretical coefficient (D_{Br}^*) for to aid in correction of diffusion coefficients for other species (Martin and Banta, 1992; Rao and Jahnke, 2004; Schulz et al., 2006).

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Using the pH-dependent equilibrium (Eq. 1), we calculated pore water NH_3 and NH_4^+ concentrations:



where the equilibrium constant ($\text{p}K_b$) is 9.25 at 25 °C; we corrected our pore water constants for ionic strength and temperature (Mulholland, 2008).

The dissolved NH_3 concentration, $[\text{NH}_3]$, can be calculated (Van Nest and Duce 1987):

$$\text{NH}_3 = \frac{[\sum[\text{NH}_x][\text{OH}^-]]}{K_b + [\text{OH}^-]} \quad (2)$$

where $[\sum\text{NH}_x]$ is for the sum of dissolved NH_3 and NH_4^+ .

Applying Fick's first law, the NH_3 , NH_4^+ and SRP fluxes were calculated by:

$$F_i = -\theta \cdot D_i x \frac{\partial C_i}{\partial x} \quad (3)$$

where F_i is the flux of different species ($\mu\text{mol cm}^{-2} \text{s}^{-1}$). The diffusion coefficient (D_i) is influenced by tortuosity (θ), temperature and sediment properties ($\frac{\partial C_i}{\partial x}$) is the gradient of nutrient concentration (C_i) and depth (x). The diffusion coefficients of NH_3 , NH_4^+ and SRP in sediments were corrected using the D_{Br} estimates, and the diffusion coefficients in a particle free solution at in situ temperature (Martin and Banta, 1992; Rao and Jahnke, 2004; Schulz et al., 2006). Percent water and the dry sediment density ($\rho \sim 2.5 \text{ g cm}^{-3}$) were used to calculate porosity (ϕ) (Boudreau, 1997):

$$\phi = \frac{(\text{water \%})}{(\text{water \%} + \frac{(1-\text{water \%})}{\rho})} \quad (4)$$

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2.7 Desorption isotherm of adsorbed ammonium (NH₄⁺-N)

In order to estimate pH effects on ammonium desorption from sediment, surface sediments were collected from Budds Landing in November 2008. Adsorbed NH₄⁺ was measured using KCl extraction (Morin and Morse, 1999). Triplicate 1 ml wet samples of the top 2 cm sediment were extracted twice with 39 ml of 2 mol L⁻¹ KCl; samples were shaken for 2 h at the field temperature (10 °C). After centrifugation and filtration, the increase in NH₄⁺ concentration relative to the blank was used to quantify adsorbed ammonium. Adsorption coefficients (*K*) were used to describe this ion exchange behavior, following Rosenfeld (1979), Mackin and Aller (1984):

$$K = \rho \cdot \frac{1 - \emptyset}{\emptyset} \cdot \frac{\hat{C}_N}{C_N} \quad (5)$$

where \hat{C}_N is exchangeable NH₄⁺ on a dry mass basis (μmol g⁻¹) and C_N is the pore water ammonium concentration (μmol L⁻¹). Porosity was measured for the top 2 cm of sediment.

To simulate response of adsorbed ammonium to pH elevation, the homogenized sediment (0–2 cm) was suspended in site water with different pH values. We added 1 ml of wet sediment to 39 ml of pH-adjusted water. To inhibit dissimilatory NO₃⁻ reduction to NH₄⁺, we used the oxygen-saturated water and left 5 ml headspace in the centrifuge tube. ΣNH_x was measured after shaking, centrifugation and filtration. Assuming a NH₃ equilibrium between the aquatic and atmospheric phase, the total release of ammonium is estimated as the sum of total dissolved ammonium in the water column ΣNH_{x(l)} and NH₃ gas within the head space (NH_{3(g)}):

$$NH_{x_{ds}} = \Delta \Sigma NH_{x(l)} + \Delta NH_{3(g)} \quad (6)$$

The headspace NH₃ was estimated from (1) the pH at the beginning and end of incubation, (2) ionic strength corrections for NH₃ (γNH₃) and NH₄⁺ (γNH₄⁺), and (3) the

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temperature-corrected Henry's law coefficient (H) (Larsen et al., 2001):

$$[\text{NH}_{(g)}] = \frac{[\sum \text{NH}_x]}{\text{RTH}_{\text{NH}_3} \left(\frac{1}{\gamma_{\text{NH}_3}} + \frac{10^{-\text{pH}}}{K_a \cdot \gamma_{\text{NH}_4^+}} \right)} \quad (7)$$

2.8 Chemical analysis

Concentrations of NH_4^+ , SRP and Fe were analyzed using colorimetric methods (Gibb, 1979; Parsons et al., 1984). Concentrations of NO_3^- , NO_2^- and pore water Br^- were determined using ion chromatography (Kopp and McKee, 1983). NO_2^- concentrations were generally very low. Dissolved N_2 and O_2 were measured by the ratios of N_2 : Ar and O_2 : Ar using membrane inlet mass spectrometry (Kana et al., 1994; Kana and Weiss, 2004). Percent water was determined as the weight loss of wet sediment after drying at 65°C . After pre-treatment with sodium hypochlorite overnight to remove carbonates and organic matter, grain size was analyzed by wet sieving and followed by pipet analysis of the remaining silt and clay (Folk, 1974).

3 Results and discussion

3.1 Physical conditions

The Powerline and Budds Landing sites had an aerobic water column, low salinity (<1), and fine grain-sized sediment (Table 1). Water depths were 0.8 m at Powerline and 1.3 m at Budds Landing. At the time of collection, bottom water pH was 9.4 at Powerline and 7.3 at Budds Landing. The temperature at Powerline (24.7°C) was similar to Budds Landing (26.9°C). Light attenuation coefficients were 4.8 m^{-1} at Powerline and 4.2 m^{-1} at Budds Landing, resulting in dim to dark conditions at the sediment surface. Both sites often have experienced cyanobacterial blooms associated with high pH in summer (Maryland Department of Natural Resources, unpublished data).

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3.2 Effect of pH on the pore water iron profile

Vertical profiles of pore water pH and iron in the Powerline cores rapidly responded to the diffusion of alkaline overlying pH into the pore water (Fig. 1a and b). The pH profile under ambient condition was nearly constant with depth and generally < 7 below 1 cm; the elevated water column pH treatments resulted in $\text{pH} > 9.0$ in the top 2 cm of sediment, decreasing downward until the pH was similar to the control. Although pH may be buffered by cation exchange (e.g. Ca^{2+} , Mg^{2+}), sulfate reduction, and anaerobic generation of acid (Cai et al., 2010), such high pore water pH's ($\text{pH} > 9.5$) have been observed during algal blooms in tidal-freshwater estuaries (Magalhaes et al., 2002). Our elevated pH profiles in sediments were similar to a time-series study of pH penetration by Bailey et al. (2006). When Potomac River sediments are incubated at pH (~ 10) in summer, high pH moves downward with time and maintains $\text{pH} > 9$ at 4 to 8 cm depth in a week incubation (Bailey et al., 2006). In our aerobic incubations, pore water Fe^{2+} was undetectable at the surface and peaked in the upper anoxic sediment horizon. Increased pH lead to a reduction in Fe^{2+} through hydroxide precipitation (Hutchins et al., 2007). As pH increased to 9.6 in the overlying water, the peak concentration of Fe^{2+} simultaneously decreased from $120 \mu\text{mol L}^{-1}$ to $68 \mu\text{mol L}^{-1}$ with its peak position shifting from 1.75 cm downward to 2.5 cm.

3.3 Effect of pH on the pore water SRP profile

Elevation of pH below the sediment-water interface resulted in SRP release into the pore water, with the peak concentrations increasing from $< 40 \mu\text{mol L}^{-1}$ to $102 \mu\text{mol L}^{-1}$ (Fig. 1d and F). Increased SRP concentrations were consistent with pH related P releases from surface metal hydroxide complexes (Seitzinger, 1991) due to the increased negative charge of mineral surfaces (Boers, 1991). Elevated pH increased upward SRP diffusion from $5 \mu\text{mol m}^{-2} \text{h}^{-1}$ under neutral pH to $39 \mu\text{mol m}^{-2} \text{h}^{-1}$ under alkaline pH treatments (Fig. 1e, f and Table 4). Under aerobic pH-neutral conditions, iron oxyhydroxides usually adsorb or co-precipitate P, hindering the flux of SRP across the

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sediment-water interface (Slomp et al., 1998). In contrast to neutral pH conditions, highly alkaline pH's enhanced pore water SRP gradients and increased the diffusion rate (Fig. 1c and f) by breaking surficial Fe-P bonds.

3.4 Effect of pH on the pore water ammonium profile

5 Under ambient pH conditions, NH_4^+ linearly increased downcore to $720 \mu\text{mol L}^{-1}$ with negligible NH_3 present (Fig. 1c). The diffusive flux rate, primarily as NH_4^+ , was $149 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Table 4). In contrast, the $\sum\text{NH}_x$ concentration in high pH cores increased to $975 \mu\text{mol L}^{-1}$ at $\sim 4 \text{ cm}$ depth (Fig. 1e). Conversion of NH_4^+ to NH_3 in surface horizons resulted in a steeper concentration gradient of NH_4^+ , increasing NH_4^+ diffusive fluxes (Table 4). Dissolved NH_3 exhibited a very sharp peak at 2–3 cm in the pH 9.6 treatment, yielding a rapid upward flux. Diffusive flux rates were the sum of $243 \mu\text{mol m}^{-2} \text{h}^{-1}$ for NH_4^+ and $234 \mu\text{mol m}^{-2} \text{h}^{-1}$ for NH_3 (Table 4). Without consideration of $\sum\text{NH}_x$ speciation at the overlying water pH 9.6, the diffusive rate calculated from the concentration gradient and diffusion coefficient of NH_4^+ was only $271 \mu\text{mol m}^{-2} \text{h}^{-1}$, less than half of the observed $\sum\text{NH}_x$ diffusive rate (Fig. 1e).

3.5 Adsorbed NH_4^+

Both pore water and adsorbed ammonium are hypothesized to be available for nitrification (Seitzinger et al., 1991). Adsorbed NH_4^+ is reversibly attracted to negatively charged binding sites on the surface of sediment particles (Rosenfeld, 1979), and can influence pore water NH_4^+ concentration as well as migration of in sediment (Morse and Morin, 2005). Without pH manipulation, the pH decreased from 7.2 to 6.5 during KCl-extraction, and adsorbed NH_4^+ in our samples averaged $3.4 \pm 0.4 \mu\text{mol g}^{-1}$. It is reasonable to expect higher adsorbed NH_4^+ in summer due to spring/summer algal deposition and the temperature-related increases in ammonification (Laima et al., 1999; Laima, 1992; Vouve et al., 2000). Our adsorption coefficient ($K = 2.6 \pm 0.4$) were similar to the observations of 2.1–7.1 in Potomac River sediments (Simon and Kennedy,

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1987) and in the upper Chesapeake Bay (Cornwell and Owens, 2011). The K value in this freshwater estuary is higher than other coastal (1.0–1.7, Mackin and Aller, 1984) and marine sediments (1.1–1.3, Rosenfeld, 1979). This result is consistent with salinity influences on NH_4^+ adsorption (Seitzinger et al., 1991b; Weston et al., 2010).

5 3.6 Effect of pH on desorption of sediment NH_4^+

Increased pH stimulated adsorbed ammonium release into pore water by converting NH_4^+ to NH_3 . The peak of dissolved NH_4^+ was $132 \mu\text{mol L}^{-1}$ at pH 9.3 (Fig. 2a). The increase of dissolved NH_4^+ at pH's 6.5–13 likely resulted from exchangeable NH_4^+ desorption. When pH approached or exceeded the P_{ka} (i.e. $\text{pH} \geq 9.25$), NH_4^+ concentrations decreased via conversion to NH_3 . This resulted in a large decrease of dissolved NH_4^+ when pH rose from 9.3 to 13 (Fig. 2a).

High pH increased the release of NH_3 and NH_4^+ , mainly from the exchangeable ammonium pool. As pH increased from 6.5 to 13 (Fig. 2b), the amount of NH_4^+ desorbed increased from 646 to 2647 nmol g^{-1} . The elevation of pH above 9.2 resulted in more than 50% of ammonium ($\sum\text{NH}_x$) converting to NH_3 (Eq. 2). Although mineral surface charges become more and more negative as pH increases, un-ionized NH_3 does not substantially adsorb to the solid phase. Moreover, drawdown of NH_4^+ concentration with pH enhancement in the aquatic phase may promote desorption until approximately 80% of KCl-extractable ammonium was desorbed (Fig. 2b).

20 3.7 Effect of pH on SRP flux

Flux rates of SRP increased with pH elevation at both stations ($P < 0.05$, student's t test). SRP efflux rates increased from $< 5 \mu\text{mol m}^{-2} \text{ h}^{-1}$ in the control, to $15\text{--}25 \mu\text{mol m}^{-2} \text{ h}^{-1}$ at pH 9.2, and to $35\text{--}55 \mu\text{mol m}^{-2} \text{ h}^{-1}$ at pH 9.6 (Fig. 3). Increased SRP flux rates with pH increases were consistent with the molecular diffusive rates of SRP estimated from pore water profiles (Table 4). In the oligohaline region of the Potomac River, SRP release from sediment increased from $< 10 \mu\text{mol m}^{-2} \text{ h}^{-1}$ in controls

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to $\sim 40 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 9.5 and $\sim 110 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 10 (Seitzinger, 1991). Similar large increases in SRP flux rates have been observed at pH's of 9.5 in freshwater sediments (Boers, 1991).

3.8 Effect of pH on DIN flux

5 For both Powerline and Budds Landing experimental cores (Fig. 4a), flux rates of $\sum\text{NH}_x$ increased significantly in the high pH treatments (especially pH > 9.5) relative to the control ($p < 0.05$, student's - t test), but differences between pH 9.2 and 9.5 were not significant. Compared to the control group, high pH (9.5–9.6) increased $\sum\text{NH}_x$ flux rates by about 6-fold at Powerline and by 2-fold at Budds Landing. Increase in $\sum\text{NH}_x$ flux rates were consistent with the pH-induced ammonium desorption at surface sedi-
10 ments and the observed changes in the pore water profile. Similar to observations of salinity-enhanced ammonium desorption (Gardner et al., 1991), ammonium desorption with alkaline pH penetration increased both the $\sum\text{NH}_x$ concentration and the proportion of NH_3 in pore-water (Fig. 1e). The conversion of NH_4^+ to NH_3 and the steeper concentration gradients of these two components all resulted in elevated $\sum\text{NH}_x$ fluxes. At Budds Landing, the flux measurements in the control were similar to the upward diffusion rate of ammonium, primarily as NH_4^+ . The measured efflux rates of $\sum\text{NH}_x$ at pH 9.6 were equivalent to the sum of the diffusive flux rate of NH_4^+ and NH_3 (Table 4). Lack of consideration of NH_3 production would result in underestimation of ammonium flux rates by 25–35 % for the flux measurement and by 50 % for the diffusive flux estimation.

Ammonium remineralization, calculated either by stoichiometric oxygen-based N remineralization or measured total inorganic nitrogen flux (i.e. $\text{NH}_4^+ + \text{NH}_3 + \text{N}_2 - \text{N} + \text{NO}_3^-$), suggests elevated pH dramatically promoted N efflux. If we assume that aerobic N remineralization stoichiometry from phytoplanktonic organic matter is 138:16
25 $\text{O}_2 : \text{N}$ and denitrification is partly fuelled by the diffusion of water column NO_3^- into sediment (Cornwell et al., 1999), $\sum\text{NH}_x$ flux accounted for 20–40 % of oxygen-based N remineralization in the control and for 68–153 % of N remineralization in the high pH

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treatments. Alternatively, if nitrogen remineralization rates were evaluated from the sum of $\sum\text{NH}_x$, NO_3^- and N_2 flux rates, pH elevation increased ammonium flux as a proportion of total N remineralization from 22 % to 105 % for sediment at Powerline and 44 % to 87 % at Budds Landing. Both estimates reveal that increased pH enhanced the proportion of ammonium release relative to the total remineralized N. However, the difference of NH_4^+ remineralization between two estimates may result from the use of O_2 consumption rates instead of CO_2 fluxes. The calculation of oxygen-based ammonium remineralization is affected by the production/ reoxidation of reduced inorganic compounds (e.g. Fe^{2+} , S^{2-} and Mn^{2+}), potential methanogenesis in organic-matter rich estuaries (Martens and Klump, 1980; Carini and Joye, 2008), and variable C:N ratios of organic matter.

No significant difference was found for NO_3^- flux rates among pH treatments ($p > 0.05$, student-t test). Fluxes of NO_3^- ranged from -70 to $10 \mu\text{mol-N m}^{-2} \text{h}^{-1}$, with most fluxes directed into the sediment (Fig. 4b). Concentrations of NO_3^- were low in the overlying water and undetectable in pore water.

3.9 Effect of pH on potential nitrification

The response of potential nitrification to pH suggests high pH (> 9) inhibited nitrification (Fig. 5a). The potential nitrification rate in the control was $84 \pm 24 \text{ nmol-N g}^{-1} \text{ h}^{-1}$, similar to rates in other fresh water sediments of $90\text{--}470 \text{ nmol-N g}^{-1} \text{ h}^{-1}$ (Cooper, 1983). With pH increasing from 9 to 11, potential nitrification rates decreased sharply from $70\text{--}110 \text{ nmol-N g}^{-1} \text{ h}^{-1}$ to below $10 \mu\text{mol-N g}^{-1} \text{ h}^{-1}$ (Fig. 5a).

Bacterially mediated nitrification is first order or zero-order kinetics with respect to $\text{NH}_4^+/\text{NH}_3$ concentrations as nitrifying substrates (Park et al., 2010). However, increases in pH can enhance $\sum\text{NH}_x$ desorption and the total inventories of exchangeable and pore water ammonium may be equal or less than controls because of NH_3 volatilization. Furthermore, pH-driven NH_3 accumulation can be toxic or inhibit the growth and enzyme efficiency of nitrifying bacteria (Anthonisen et al., 1976; Kim et al.,

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2006). In laboratory observations and modeling, both high pH and NH_3 have negative effects on nitrifying bacteria, ammonium-oxidizing bacteria (AOB, *Nitrosomonas*) and nitrite-oxidizing bacteria (NOB, *Nitrobacter*) (Van Hulle et al., 2007). Elevation of pH above 9 could inhibit enzyme activity of AOB and NOB since the optimal pH range is 6–8.5 for AOB and 5.5–8 for NOB (Van Hulle et al., 2007; Park et al., 2010). Even though nitrifying bacteria might survive out of the optimal pH range, they would pay an energy cost to maintain their cytoplasmic pH (Wood, 1988).

Although few field studies have been conducted on the effect of pH on sediment nitrification relative to water column and soil environments (Simek et al., 2002; Carini and Joye, 2008), sediment potential nitrification rates appear to be limited by high pH (> 8) in freshwater and were positively related to exchangeable NH_4^+ in 36 stream surveys (Strauss et al., 2002). Elevated pH inhibition of nitrification, with decreases of 80 % at pH 9 relative to peak nitrification, have been observed in fine-grained sediment in the Arika Sea (Isnansetyo et al., 2011).

3.10 Effect of pH on nitrification rates

Elevated pH negatively impacted the intact-core nitrification as measured by the changes in $\sum\text{NH}_4^+$ or NH_4^+ flux rates after adding CH_3F , an inhibitor of ammonium oxidation (Fig. 5b). Under neutral conditions, no significant difference of nitrification rates existed between the evaluation from $\sum\text{NH}_4^+$ flux ($182 \pm 49 \mu\text{mol m}^{-2} \text{h}^{-1}$) and from NH_4^+ flux ($210 \pm 35 \mu\text{mol m}^{-2} \text{h}^{-1}$). Sediments in the upper Sassafras River show considerably higher nitrification rates than the $< 40 \mu\text{mol m}^{-2} \text{h}^{-1}$ typical of the mesohaline region of the Chesapeake Bay in summer (Kemp et al., 1990), reflecting the aerobic overlying water conditions.

Similar to nitrification potentials (Fig. 5a), increasing pH from neutral to 9.5 exerted a remarkable depression on nitrification, as evidenced by the >50 % reduction in nitrification under alkaline water (Fig. 5b). If both dissolved NH_4^+ and adsorbed NH_4^+ in sediments are assumed to be the main substrates for nitrification (Seitzinger et al., 1991), high pH related decreases in N availability could functionally suppress nitrification. The

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reduction of NH_4^+ concentration in pore water as well as its proportion to $\sum\text{NH}_x$ may reduce the ammonium availability for nitrification. As a negative function of pH (Fig. 2), adsorbed NH_4^+ may be reduced, possibly decreasing nitrification (Fig. 5). Following pH penetration into the aerobic sediment surface (typically ~ 2 mm), NH_3 toxicity could suppress nitrification (Isnansetyo et al., 2011). In addition, nitrifying bacteria are obligate chemoautotrophs and grow with inorganic carbon in the form of CO_2 as their sole carbon source (Staner, 1970); a reduction in CO_2 with pH elevation may therefore potentially inhibit nitrifying metabolism.

3.11 Effect of pH on denitrification

In aerobic Chesapeake Bay sediments, alternative N_2 production via annamox appears inconsequential (Rich et al., 2008), with coupled nitrification-denitrification being the key pathway to transform the rematerialized nitrogen to N_2 -N (Cornwell et al., 1999). Coupled nitrification-denitrification decreased from $180\text{--}280 \mu\text{mol-N m}^{-2} \text{h}^{-1}$ to less than $85 \mu\text{mol-N m}^{-2} \text{h}^{-1}$ as the overlying water pH increased to 9.6 (Fig. 6). Denitrification efficiency, the percentage of inorganic nitrogen released from the sediment as N_2 -N (Heggie et al., 2008), decreased from 84 % to 35 % at Powerline and 64 % to 17 % at Budds Landing.

Reduction in denitrification with pH elevation may be a consequence of limited NO_3^- supply and alkaline pH constraint on denitrifying bacterial activity. The NO_3^- supply for denitrification may come from ammonium oxidation and diffusion from the overlying water. In this study, the NO_3^- supply from the overlying water (Table 1) was low relative to denitrification rates, an observation consistent with undetectable pore water NO_2^- and NO_3^- concentrations. Hence, consistent with pH suppression of nitrification (Fig. 5), denitrification at high pH is likely limited by the NO_3^- supply (Fig. 6). Moreover, the optimal pH range for denitrification is 7–8 in soil and anaerobic sediments (Simek et al., 2002); higher pH may directly inhibit the activity of denitrifying bacteria. Nitrate reducing bacteria, such as *Thioalkalivibrio nitratireducens*, can survive in alkaline

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sediment and cultivation media at pH 10. However, the nitrite reductase activity of *T. nitratireducens* was maximal when pH ranged from 6.7–7.5, and 80 % of the activity was inhibited at high pH (9–10) (Filimonenkov et al., 2010).

Although dissimilatory nitrate reduction to ammonium (DNRA) in freshwater sediments appears to be minor relative to denitrification (Scott et al., 2008), DNRA usually occurs when NO_3^- inputs exceed the availability of carbon substrate for denitrification (Tiedje et al., 1989). As a consequence of pH elevation, limited NO_3^- consumption through anaerobic denitrification may provide the potential chances for DNRA and enhance ammonium production. However, DNRA may play a minor role in explaining the enhanced ammonium fluxes. We did not expect high DNRA occurs in the Sassafra River sediment with undetectable free sulfide concentrations.

3.12 Effect of pH on oxygen consumption

Oxygen consumption rates in the controls were higher in July at Budds Landing than in June at Powerline, partly a result of the promoted bacteria efficiency of organic matter decomposition with rising temperatures. However, oxygen consumption decreased as pH increased at both sites (Fig. 6). This is likely related to the alkaline pH effects on bacteria production and respiration (Tank et al., 2009). Assuming pH has no effect on organic matter remineralization to ammonium at each sampling site, we postulate that inhibition of nitrification by increased pH resulted in the reduction of oxygen consumption.



The molar ratio of O_2 to $\sum\text{NH}_4^+$ is 2 for nitrification. The measured slopes of $\Delta\sum\text{NH}_4^+$ and $-\Delta\text{O}_2$ fluxes were consistent with nitrifying stoichiometry (Fig. 7), which suggests high pH increased sediment $\sum\text{NH}_4^+$ diffusion into overlying water rather than enhancing coupled nitrification-denitrification. Deviation of the $-\Delta\text{O}_2:\Delta\sum\text{NH}_4^+$ flux rates from the theoretical 2:1 ratio may result from variation in sediment cores, such as oxidation of

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Mn (II) and Fe (II), and sediment buffering effects on OH⁻ penetration in depth and magnitude.

4 Conclusion and ecological implications

Harmful algal blooms, including cyanobacterial blooms, present a clear challenge to the functioning of shallow water coastal ecosystems. Like other blooms, cyanobacterial blooms are increasing in frequency and magnitude over time due to eutrophication. Cyanobacterial blooms can be locally persistent and extensive. However, determining the cause of such blooms can be elusive. Elevated temperature, a long water residence time, and availability and proportions of inorganic and organic nutrients are often cited as “triggers” (Glibert, 2011). Mitigation efforts for eutrophication have not always had success in hindering the development of harmful algal blooms (Glibert, 2011). Indeed, cyanobacterial blooms are common in the Potomac River (Chesapeake Bay) despite considerable progress removing P from point sources (Krogmann et al., 1986; Ruhl, 2010)(Krogmann et al., 1986; Ruhl and Rybicki, 2010). The occurrence of blooms during drought periods with low external nutrient inputs suggests that internal nutrient recycling is a key to the initiation and sustainability of cyanobacterial blooms.

Nutrient release from bottom sediments can be a substantial source in shallow water ecosystems, potentially satisfying nutrient demand of algal growth and enhancing eutrophic conditions. High rates of photosynthesis during dense blooms promote a large water column pH increase, especially in the low pH buffering water such as lake and freshwater estuaries.

Nutrients, especially N, are limiting to primary production during the extensive summer blooms in Chesapeake Bay (Kemp et al., 2005). In summer, bloom forming cyanobacteria are dominant by diazotrophs, resulting in high pH persistence in the tidal fresh Sassafras River (O’Neil and Maryland DNR, unpublished data). Our study suggests pH elevation can increase inorganic N supply from the sediment into the water column. As pH increased above 9, the N flux from sediments was more than doubled by

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5 promoting NH_4^+ and NH_3 flux and inhibiting N_2 loss. Even though N_2 -fixing cyanobacteria can survive during N deficiency, they prefer to take up dissolved inorganic N rather than consuming energy for N_2 fixation (Paerl, 2008). The pH-induced release of ammonium from sediments may thereby be an important N source for primary productivity during dense blooms in shallow estuaries or lakes. The molar ratio of DIN: SRP sediment efflux decreased from >70 to 9–12 when experimental pH rose from neutral to above 9, which may reinforce N limitation and selectively support N_2 -fixing cyanobacterial blooms. Given higher P demand for diazotrophs, the augmentation of P flux with pH may boost the growth and persistence of algal blooms (Xie and Xie, 2003; Paerl, 2008).

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Table 1. Sediment grain size, ambient dissolved nutrients in water column and the flux rates before pH modification. Samples were collected at the Powerline on 18 June 2008 and Budds Landing on 14 July 2009. Grain size measurements were conducted after flux experiments; other measurements are average nutrient concentrations \pm SE ($n = 3$) and average flux rates \pm SE ($n = 4 - 9$). Negative rates indicate uptake by the sediment.

Variables	Powerline	Budds landing
Grain size (%)		
sand	3.2	6.7
silt	59.9	58.8
clay	36.9	34.4
Bottom water characterization		
SRP ($\mu\text{mol L}^{-1}$)	0.7 ± 0.04	0.23 ± 0.07
$\text{NH}_4^+\text{-N}$ ($\mu\text{mol L}^{-1}$)	2.1 ± 0.05	0.6 ± 0.1
$\text{NO}_3^-\text{-N}$ ($\mu\text{mol L}^{-1}$)	7.5 ± 0.02	0.82 ± 0.02
Salinity	0.05	0.2
Temperature ($^{\circ}\text{C}$)	24.7	26.9
pH	9.4	7.3
DO (mg L^{-1})	10.3	12.48
DO (%)	127.4	158.2
Chl- <i>a</i> (mg L^{-1})	78	46.5
Core fluxes		
$\text{NO}_3^-\text{-N}$ flux ($\mu\text{mol-N m}^{-2} \text{hr}^{-1}$)	-41 ± 0.2	10 ± 18
$\text{NH}_4^+\text{-N}$ flux ($\mu\text{mol-N m}^{-2} \text{hr}^{-1}$)	62 ± 8.5	310 ± 32
SRP flux ($\mu\text{mol-P m}^{-2} \text{hr}^{-1}$)	-0.2 ± 1.2	5.0 ± 3.7
N_2 flux rate ($\mu\text{mol-N m}^{-2} \text{hr}^{-1}$)	259 ± 38	176 ± 21
O_2 flux rate ($\mu\text{mol-O}_2 \text{m}^{-2} \text{hr}^{-1}$)	-1614 ± 62	-2240 ± 293

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Table 2. Experimental overlying water pH's for experimental incubations of cores from the Powerline ($n = 4$) and Budds Landing sites. The Powerline incubations had a sequential change of pH while the Budds Landing incubations had 3 replicate cores at 3 different pH's. For Budds Landing, $n = 3$ at each pH level except for the control on the first day when $n = 9$. pH data is the mean value (\pm SE).

Treatment	Powerline		Budds Landing	
	Time (day)	pH	Time (day)	pH
Control	1st	7.8 ± 0.01	1st and 7th	7.4 ± 0.3
pH1	6th	9.2 ± 0.02	7th	9.2 ± 0.05
pH2	11th	9.6 ± 0.03	7th	9.5 ± 0.2

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Table 3. The kinetic parameters used in calculation of diffusion rates and in calculation of ammonium adsorption-desorption in Budds Landing sediments.

Parameter	Value	Comments	Ref.
pKb	9.25		
Temperature	27.0 °C		
For calculation of the molecular diffusive rates			Stumm and Morgan (1996)
water %	74 %	Top 10 cm sediments	
ρ	2.50	g cm^{-3}	
\emptyset	0.88		
θ^2	1.26		
$D^* \text{-Br}^-$	20.10	The diffusion coefficient in free solution ($D^*: 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	Li and Gregory (1974)
$D^* \text{-PO}_4^{3-}$	5.77		
$D^* \text{-NH}_4^+$	19.80		
$D^* \text{-NH}_3$	24.52		
$D \text{-Br}^-$	1.09	The corrected diffusion coefficient	
$D \text{-SRP}$	0.30	($D: 10^{-6} \text{ cm s}^{-1}$)	
$D \text{-NH}_4^+$	1.02		
$D \text{-NH}_3$	1.29		
For adsorption coefficient of ammonium at top 2 cm sediment			
water %	89 %	top 2 cm	
\emptyset	0.95	top 2 cm	
\hat{C}_N	1.5 ± 0.2	$\mu\text{mol g}^{-1}$ wet sediment	
C_N	0.07	$\mu\text{mol mL}^{-1}$	
For ammonium desorption			
R	8.21×10^{-5}	$\text{atom m}^3 \text{ mol}^{-1} \text{ K}^{-1}$	Larsen et al. (2001) Capone et al. (2009)
$H \text{-NH}_3$	7.05×10^{-2}	$\text{mol atm}^{-1} \text{ m}^{-3}$	
$H^s \text{-NH}_3$	1.64×10^{-3}	RTH-NH ₃	
I	1.47×10^{-3}		
Y_{NH_3}	1.00		
$Y_{\text{NH}_4^+}$	0.88		

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Table 4. Efflux rates of SRP and $\sum\text{NH}_x$ in control and in high pH treatments in sediment cores from Budds Landing. Net flux rates were compared to rates estimated from molecular diffusion of pore water.

pH level	SRP flux rates ($\mu\text{mol-P m}^2 \text{h}^{-1}$)		Ammonium flux rates ($\mu\text{mol-N m}^2 \text{h}^{-1}$)			
	Diffusive rate	Flux rate	NH_4^+	Diffusive rate NH_3	$\text{NH}_4^+ + \text{NH}_3$	Flux rate $\sum\text{NH}_x$
Control	4.6	3 ± 3.2	149.5	0.2	149.7	61.7 ± 8.5
pH = 9.6	39.2	43.5 ± 7.4	243.1	234.2	477.3	440.9 ± 19.1

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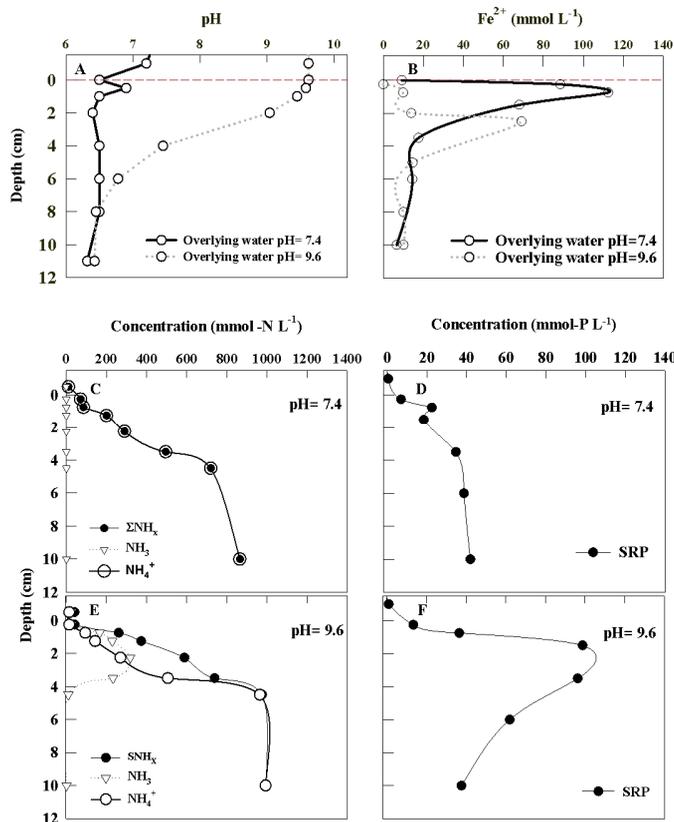


Fig. 1. Budds Landing porewater profiles in the upper 10 cm of sediment under high pH (9.6) and normal pH (7.4) treatments, including vertical changes of pH (**A**), porewater Fe (**B**), SRP (**D**, **F**), and ΣNH_x (**C**, **E**). Changes in ammonium speciation, resulted from surface pH elevation, were calculated by the equilibrium of NH_3 and NH_4^+ .

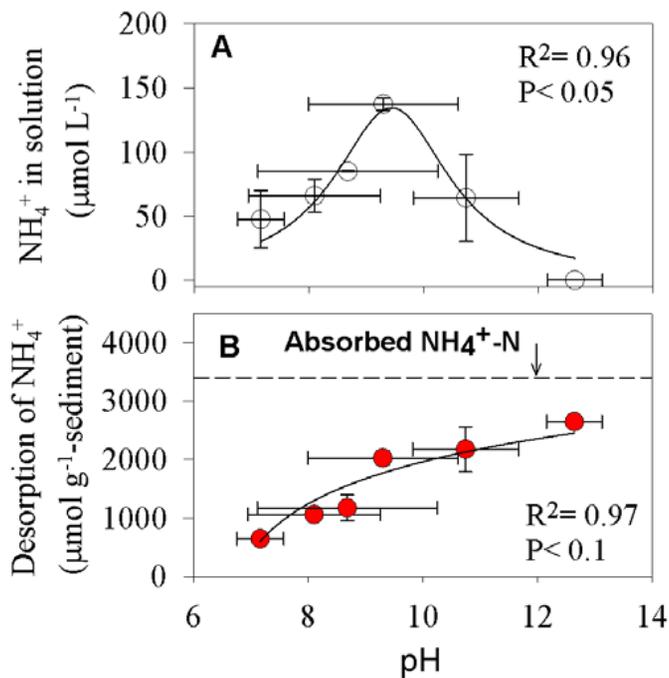


Fig. 2. Experimental pH effects on NH_4^+ concentration in solution (**A**) and desorption of exchangeable NH_4^+ (**B**), using the 0–2 cm homogenized sediments from Budds Landing collected in November 2008. Dissolved NH_4^+ concentration was estimated from the $\sum\text{NH}_x$ concentrations and pH in the aquatic phase. Desorbed NH_4^+ was the sum of $\sum\text{NH}_x$ in water and the volatilized NH_3 in the headspace of the sealed centrifuge tubes. The dashed line represents “total” absorbed NH_4^+ , estimated by KCl extraction of pH-neutral sediment.

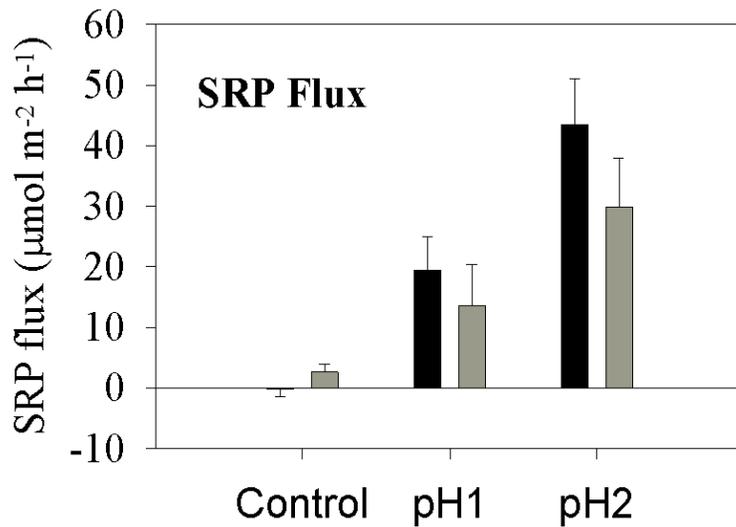


Fig. 3. Experimental pH effects on SRP flux rates from sediments at Powerline (black bars) and Budds Landing (gray bars). Error bars are the standard deviation.

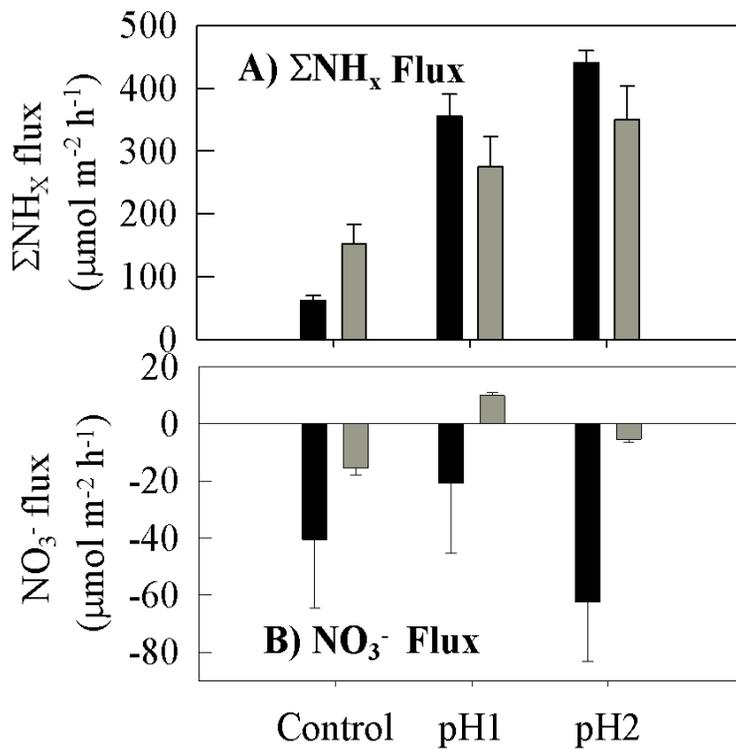


Fig. 4. Experimental pH effects on flux rates of total ammonium and nitrate. Sediment cores were taken from Powerline (black bars) and Budds Landing (gray bars). Data are presented as mean flux rates \pm standard deviation.

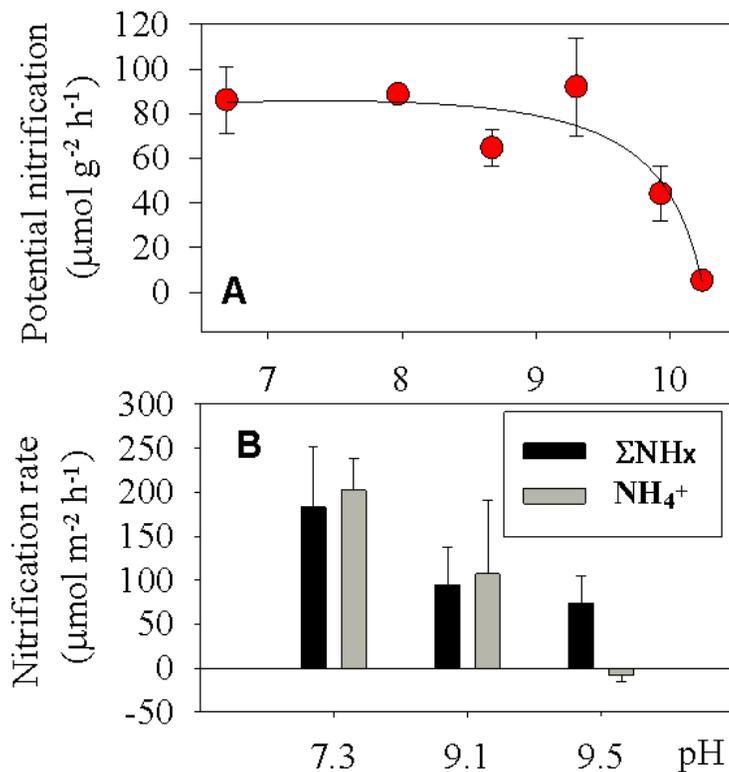


Fig. 5. Experimental pH effects on potential nitrification **(A)** and intact core nitrification rates **(B)** from Budds Landing in July 2009. The potential nitrification rates **(A)** are calculated from nitrate production in NH_4^+ -amended slurries from surficial sediments (0–2 cm). Nitrification rates **(B)** are estimated by inhibition of nitrification using CH_3F . Bars show the average flux rates of ΣNH_x^+ (black bars) and NH_4^+ (gray bars) as well as the standard error for triplicate samples.

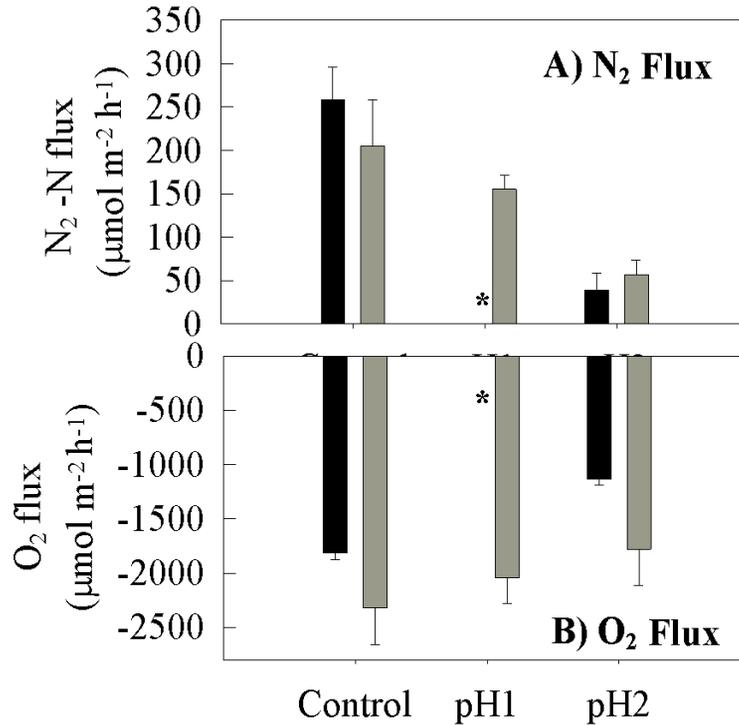


Fig. 6. Experimental pH effects on denitrification rates **(A)** and oxygen consumption rates **(B)** of sediments from the Powerline (black bar) and Budds Landing (grey bar) sites. “*” indicates where measurements were not taken. Bars show the mean of triplicate cores, error bars are the standard error.

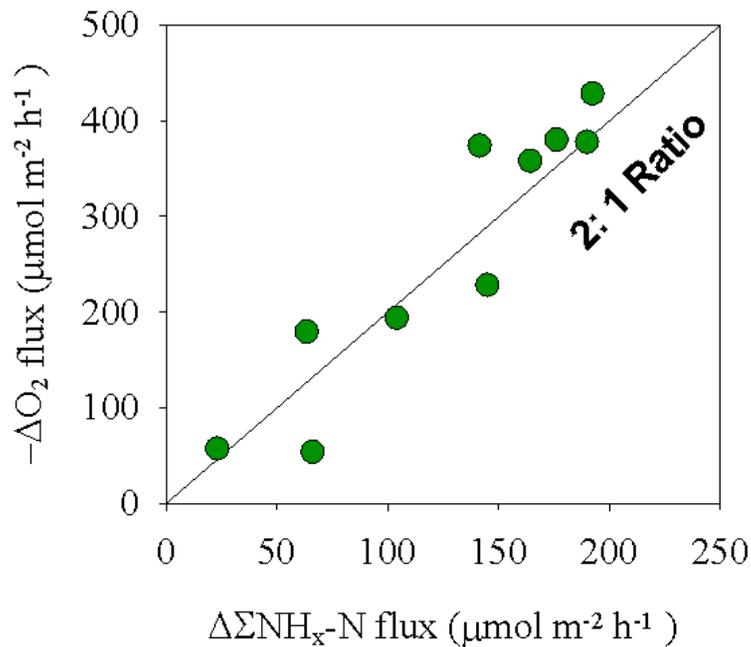


Fig. 7. The relationship between the increased ΣNH_x fluxes and the reduced oxygen consumption rates after pH elevation. Data from Powerline are the changes of ΣNH_4^+ and O_2 flux rates in the same core after pH was elevated from 7.8 to 9.5. Data from Budds' Landing are the changes of flux rates between control cores and cores at a pH of 9.2 and 9.5 after 6 days incubation. The slope (K) of solid line is 2:1, which is equal to the molar ratio of ammonium to oxygen for nitrification (Eq. 8).

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