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Vertical Dissolved Inorganic Nitrogen Fluxes in Marsh and Mudflat Areas of the Yangtze Estuary

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Nitrogen (N) is a dominant macronutrient in many river-dominated coastal systems, and excess concentrations can drive eutrophication, the effects of which can include hypoxia and algal blooms. The Yangtze River in China transports a large amount of dissolved inorganic N. Therefore, it is important to understand the role of the marsh and mudflat areas within the estuary on processing this exogenous N load. In situ dissolved inorganic nitrogen (DIN) fluxes across the sediment–water interface were determined monthly at Chongming Island at two sites (a vegetated marsh and an unvegetated mudflat) and were compared with rates from a previously published laboratory incubation study by our research group. Results from the in situ study showed that NO_3^- flux rates comprised the major component of total DIN flux, ranging from 55 to 97%. No significant difference was observed in the N flux rates between the marsh and mudflat sites. Overall, sediment at both sites served as a sink of DIN from surface water with mean flux rates of −178 μmol m^{-2} h^{-1} and −165 μmol m^{-2} h^{-1} for the marsh and mudflat, respectively. In general, DIN flux rates were not significantly correlated with DIN concentrations and other measured parameters (temperature, dissolved oxygen, salinity, and pH) of surface water. The in situ measured fluxes of NO_3^- and NO_2^- in this study were not significantly different from those of our previous laboratory incubation ($p > 0.05$), whereas NH_4^+ fluxes in situ were significantly lower than those from the laboratory core incubations ($p < 0.05$). This result suggests that caution should be used when extrapolating rates from laboratory incubation methods to the field because the rates might not be equivalent.

Increased production and use of artificial fertilizers, fossil fuels, and leguminous agriculture worldwide have dramatically increased the amount of bioavailable N in the environment by an order of magnitude since the Industrial Revolution (Galloway et al., 2008). This anthropogenic stimulation of the N cycle has led to a number of environmental problems (Galloway et al., 2008). One typical problem is the ever-increasing amount of NO_3^- discharged by rivers into coastal systems (Taylor and Townsend, 2010; Roy et al., 2013). Consequently, estuaries, many of which are located in highly populated and industrialized regions of the world, receive high loading of nutrients that have great potential to degrade water quality and affect aquatic resources (Bricker et al., 2008; White et al., 2009). This bioavailable N load contributes to algal blooms and associated coastal hypoxia, which have important consequences for these dynamic and productive systems (Bargu et al., 2011; Roy et al., 2013).

Estuarine marsh soil and tidal mud flat sediment can play a critical role in improving estuarine water quality by acting as a sink of bioavailable N. Although some studies have found that sediment can act as an efficient nutrient sink (Stockenberg and Johnstone, 1997; Barnes and Owens, 1999; Onken and Riethmüller, 2010), other studies have found that sediment can be a N source, releasing inorganic N into surface waters (Jickells, 1998; Malecki et al., 2004; Deborde et al., 2008). Establishing the magnitude and direction of DIN fluxes across the sediment–water interface is important for understanding coastal N cycling and for determining the role of estuarine sediment and marsh soil in transforming and removing the exogenous DIN load from coastal waters.

Coastal marsh soil and tidal mudflat sediment generally present different physical and chemical properties due to differences in hydrodynamic conditions imposed by tidal submergence and in the presence and absence of vegetation as well as associated microbial activity within the rhizosphere (Yang et al., 2008; Kirby, 2010; VanZomeren et al., 2013). Fluctuations in temperature, salinity, and N concentrations of surface water can affect microbial activity linked to N cycling (Wang et al.,

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Abbreviations: DIN, dissolved inorganic nitrogen; LOI, loss on ignition; DO, dissolved oxygen.

2007; Putnam-Duhon et al., 2012). These factors, along with differences in the soil/sediment characteristics, may affect DIN exchanges across the sediment–water interface (Denis et al., 2001; Spears et al., 2008) and determinations as to whether a particular site serves as a sink or source for N over time (Denis et al., 2001).

The vast majority of studies on N sediment–water fluxes in coastal systems have been conducted using field chambers or intact cores performed in the laboratory and, more importantly, with very few time points throughout the year (Denis et al., 2001; Malecki et al., 2004; Spears et al., 2008). The importance of measuring DIN flux rates seasonally is linked to the unbalanced timing of DIN loading to coastal regions over the year (Rabalais et al., 2002). Therefore, the goal of this study was to determine the monthly in situ DIN flux rates at marsh and bare tidal mud flat sites to examine the magnitude and direction of DIN flux rates across the sediment–water interface seasonally. We then compared our in situ DIN flux rate determinations with those from a previously published laboratory incubation flux study for Yangtze estuary sediments to determine how well the laboratory rates mimicked rates determined in the field.

Materials and Methods

Study Site

Chongming Island is located in the Yangtze estuary, within the northern subtropical monsoon zone, and is subject to four distinct seasons. Annual mean tide water temperature is approximately 17.5°C, ranging from ~28°C in August and ~ 6.7°C in January (Jin et al., 2007). The average inorganic N concentrations in the water of Yangtze River in recent years have ranged from 1.40 to 20.0 μmol L^{-1} for NH_4^+ and from 0.10 to 2.50 μmol L^{-1} for NO_2^- and averaged 68.0 μmol L^{-1} for NO_3^- (Xiao et al., 2007). The Yangtze River discharges a large amount of suspended sediment into the Yangtze estuarine area, which drives formation of the islands and coastal tidal flats (Liu et al., 2007). The eastern portion of Chongming Island is the largest marsh-tidal flat zone in the Yangtze estuary located outside the east dike of Chongming Island and is subjected to surface water exchange through tidal action. This location has extensive areas of unvegetated mudflat and includes vegetated tidal marsh colonized primarily by *Scirpus mariqueter*, *Phragmites communis*, and *Spartina alterniflora*. At the central section of this region, sampling sites (one marsh and one tidal mudflat) were established for monthly sampling evenly distributed over 1 yr (Fig. 1). The length of time of submergence for each sampling site varies from about 1 h to >8 h, depending on the period of tidal cycling shift from neap to spring over a month.

Flux Measurements

An in situ field incubation chamber was designed for investigating the exchange of DIN (NH_4^+, NO_3^-, and NO_2^-) across the sediment–water interface (Fig. 2). The flux chamber was composed of four small cylindrical cells made of Perspex. Three of the cells, to provide for triplicate measurements, were used for determining sediment–water interface exchange (Φ: 160 mm; L: 600 mm), and the fourth was used as the water column control (Φ: 160 mm; L: 550 mm). The top of each cell was outfitted with a screw cap that included a rubber membrane to prevent the leakage of air and water during incubation. A pump was also provided in each cell to gently mix the water column to prevent stagnation and to more closely mimic the movement of the surface water (Fig. 2). The incubation setup was held fixed in place by a rigid steel frame and black nylon net for the 5-h incubation. The surface water contained high levels of suspended sediment; consequently, in combination with the black netting, light availability to the sediment surface in the chambers was low.

Monthly sampling was performed during the time of tidal submergence of the mudflat sediment and marsh soil. Before the incoming tide submerged the sampling sites, the cells were inserted at least 50 mm into sediment. The control cell, which

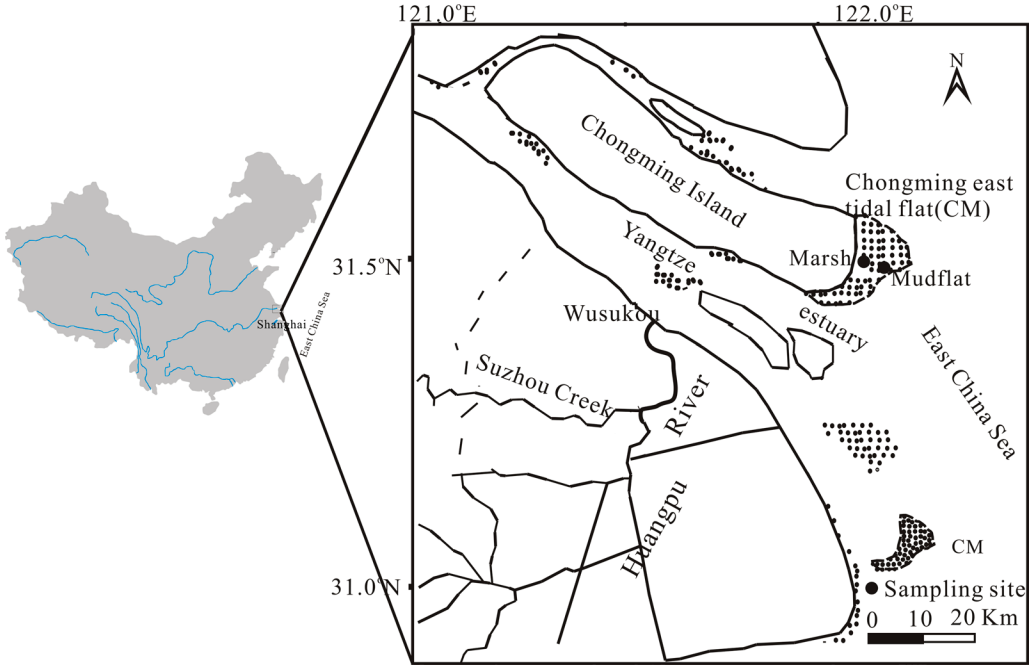

Fig. 1. Map of the Yangtze estuary including locations of the sampling sites. CM, Chongming east tidal flat.

was sealed on the bottom, was placed on the sediment surface. When the tide water began to submerge the sampling site, 2 L of surface water was slowly fed into each cell, and then each cell was closed with an airtight lid. At the beginning and end of the incubation, 40-mL water samples were collected from each cell by syringe and immediately filtered through 0.45-μm syringe filters. The pH, dissolved oxygen (DO), salinity, and temperature of surface water were determined by YSI 550A and YSI 30 (YSI Inc.).

One 10-cm sediment core (Φ: 50 mm) was collected from each site at the end of the incubation for determination of sediment characteristics. Water and sediment samples were placed on ice in a cooler and transported to the laboratory for analyses.

Analytical Procedures

At the laboratory, sediment cores were cut into 1-cm-thick slices. Subsamples were weighed and then dried at 105°C for 24 h to determine moisture content, followed by combustion of a subsample at 550°C for 5 h to determine weight percent organic matter by loss on ignition (LOI) (Heiri et al., 2001). The grain size of the sediment was measured by a laser granularity analyzer (LS 13 320, Beckman Coulter Inc.). A 1 mol L^{-1} KCl extraction was used to determine extractable NH_4^+ concentrations by shaking sediment (5 g, wet weight) with 50 mL of KCl for 1 h, followed by filtering through 0.45-μm filters and storage at 4°C until analysis (VanZomeren et al., 2012). The concentrations of extractable NH_4^+ in sediment and NO_3^-, NO_2^-, and NH_4^+ in surface water were determined by colorimetric techniques (Grasshof et al., 1983).

Fluxes of DIN across the sediment–water interface were calculated based on the concentration changes between the beginning and end of incubation after Aller et al. (1985):

$$F = V_t(C_t - C_0)A^{-1}T^{-1} \quad [1]$$

where F is the N flux (μmol m^{-2} h^{-1}), V_t the total volume of surface water at time t in the chamber (L), A is the surface sediment of exchange (m^2), C_t and C_0 are DIN concentrations at time t and 0, and T is the incubation time (h). We adopted the convention that flux from the sediment to the water column was considered positive, and negative values represented a sink to the sediment.

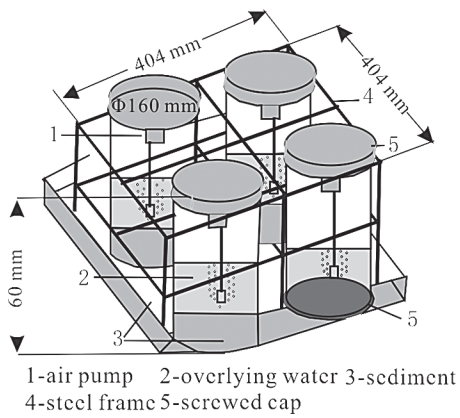

Fig. 2. Diagram of field incubation apparatus used for determining field flux rates.

Statistical Procedures

The Shapiro-Wilk test was used to assess the normality of the data, and the results showed that all data were normally distributed ($p > 0.05$). Sediment characteristics, flux rates between sites and time, and differences between the DIN fluxes in situ and from laboratory incubations were compared using ANOVA. Pearson product moment correlations were calculated for DIN fluxes, surface water nutrient concentrations, and sediment characteristics.

Results

Surface Water Characteristics

The monthly pattern of basic physiochemical parameters and N concentrations in surface water is illustrated in Fig. 3. The mean ± SD of annual surface water temperature, salinity, DO, and pH were 18.5 ± 9.7°C, 8.4 ± 8.2‰, 9.5 ± 1.9 mg L^{-1}, and 7.97 ± 0.33, respectively. Warming of the water began in spring and reached a maximum in late summer. In winter, temperature

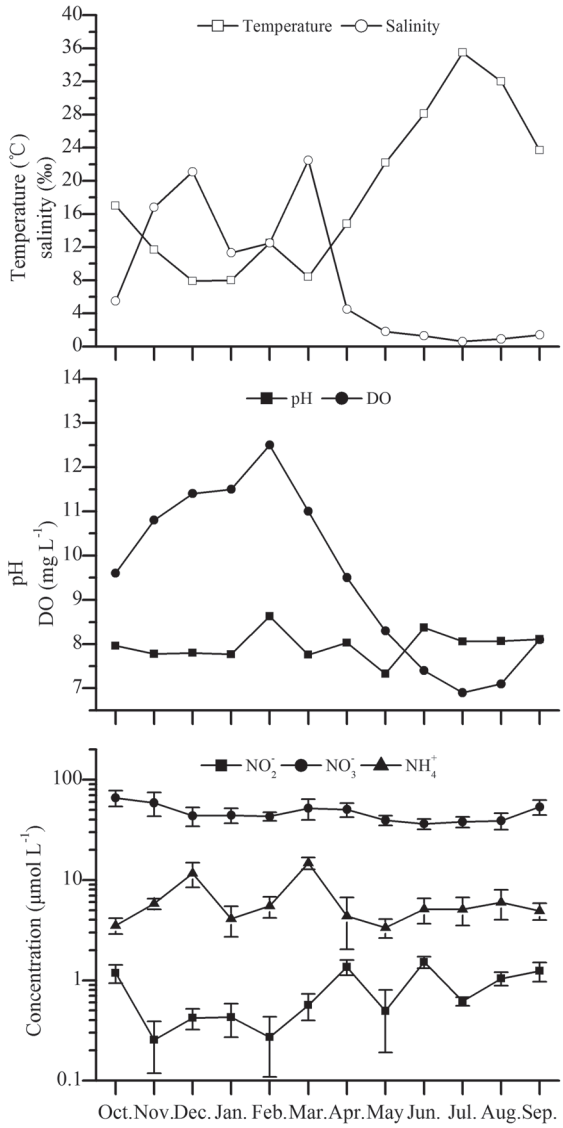

Fig. 3. Monthly temperature, salinity, pH, dissolved oxygen (DO), nitrite (NO_2^-), ammonium (NH_4^+), and nitrate (NO_3^-) concentrations of surface water (error bars represent SD; $n = 3$).

dropped to as low as 7.9°C. However, monthly shifts in salinity and DO were opposite to that of water temperature. The pH measurements did not demonstrate any significant shifts over the year.

The concentrations of NO_2^-, NO_3^-, and NH_4^+ in the surface water were 0.78 ± 0.45, 47.0 ± 9.20, and 6.2 ± 3.45 μmol L^{-1}, respectively, and ranged from 0.26 to 1.52, from 36.2 to 66.0, and from 3.4 to 14.8 μmol L^{-1}, respectively (Fig. 3). The NO_3^- concentrations comprised from 77.2 to 93.3% of the total amount of DIN in the surface water. Concentrations of NH_4^+, on average, made up 11.4% of DIN, whereas NO_2^- concentrations accounted for only 1.50% of DIN over the year. Monthly variations of DIN concentrations in surface water were observed, in particular for NO_2^- and NH_4^+ (Fig. 3).

Temperature was significantly negatively correlated with salinity and DO (Table 1). The NO_3^- and NH_4^+ concentrations had significantly negative correlation with temperature, whereas NO_2^- concentrations and temperature were positively correlated. The NH_4^+ concentrations were positively correlated with salinity, and NO_2^- concentrations were negatively correlated with salinity and DO (Table 1).

Sediment Characteristics

Sediments of Chongming eastern tidal flat have been reported to be primarily influenced by particulate input from the Yangtze River (Liu et al., 2006) and were classified as fine sand, silty sand, and silt (Wei et al., 2007). The sand fraction of the sediment generally dominated the grain size of the vegetated marsh and the mudflat (Table 2). Mean grain size of sediment in the mudflat was significantly coarser than that of the marsh, at 39.1 ± 15.5 μm and 29.3 ± 5.0 μm, respectively, across all sampling dates. The LOI is indicative of the amount of organic matter in soils and sediments (Walter and Dean, 1974). There were no significant differences in the average annual values of LOI between marsh soil (3.11 ± 0.70%) and mud flat sediment (3.19 ± 0.98%). The LOI in marsh soil was highest in June, and lower LOI values were observed from July to September. Regarding mud flat sediment, LOI was much higher from February to June than in the other months (Fig. 4). Vertical patterns in extractable NH_4^+ concentrations in sediments of the tidal flat showed a general linear increase with increasing depth (Fig. 4). There were significantly higher concentrations of extractable NH_4^+ at each depth of sediment in the mudflat than in the marsh ($p < 0.05$).

Dissolved Inorganic Nitrogen Flux Rates

The NO_2^- fluxes had low variability, ranging from −20.8 to 5.55 μmol m^{-2} h^{-1} (−4.30 ± 8.71 μmol m^{-2} h^{-1}) for the marsh sites and from −7.5 to 9.8 μmol m^{-2} h^{-1} (−1.25 ± 5.26 μmol m^{-2} h^{-1}) for the mudflat (Fig. 5). The NO_3^- fluxes had significant variability over time, ranging from −427.6 to 331.7 μmol m^{-2} h^{-1} at the marsh site and from −407.7 to 375.4 μmol m^{-2} h^{-1} at the mudflat sites. In general, NO_3^- diffused from the surface water into the sediment, with mean influx rates to the sediment of −145.9 ± 240.9 μmol m^{-2} h^{-1} and −171.0 ± 202.8 μmol m^{-2} h^{-1} for the marsh and mudflat, respectively (Fig. 5).

The marsh NH_4^+ fluxes ranged from −131.5 to 82.1 μmol m^{-2} h^{-1} (mean, −27.5 ± 67.9 μmol m^{-2} h^{-1}) and generally diffused into the sediment at the marsh except for July, August, and October. The average direction of NH_4^+ diffusion at the mudflat site was out of the sediment and into the surface water in October, November, February, June, and July (Fig. 5). Values ranged from −71.0 to 239.1 μmol m^{-2} h^{-1} (annual mean, 23.3 ± 86.4 μmol m^{-2} h^{-1}). The NO_3^- fluxes accounted for between 55 and 97% of the total DIN flux rates, so trends in DIN flux over time generally followed NO_3^- fluxes at both sites. On average, the mudflat and marsh sites served as a sink for total DIN from the surface water to the tidal flat sediment and marsh soil (mudflat, −164.9 ± 204.9 μmol m^{-2} h^{-1}; marsh, −177.7 ± 245.1 μmol m^{-2} h^{-1}). There were no significant differences for NO_2^-, NO_3^-, NH_4^+, and DIN fluxes between the marsh and mudflat sites over the year, suggesting that both environments provide adequate physiochemical conditions for removal of DIN from surface waters.

The results of correlation analyses between DIN fluxes, surface water nutrient concentrations, and other physicochemical parameters are presented in Table 3. At the marsh site, NH_4^+ flux rates were positively correlated with water temperature but negatively correlated with salinity and DO, whereas NO_2^- flux rates were negatively correlated with the surface water NO_2^- concentration. At the mudflat site, only NH_4^+ flux rates were significantly correlated with the NH_4^+ concentrations in surface water.

Table 1. Pearson product moment correlation coefficients between nutrient concentrations and water quality parameters of the surface water (*n* = 12).

Parameters	NO_2^-	NO_3^-	NH_4^+	Temperature
Temperature	0.473*	−0.451*	−0.419*	–
Salinity	−0.631*	0.295	0.766*	−0.841*
pH	0.320	−0.145	−0.135	0.235
Dissolved oxygen	−0.618*	0.339	0.369	−0.936**

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

Table 2. Grain size distribution of the sediment at each site.

Grain size	Marsh			Mudflat		
	Mean	Range	SD	Mean	Range	SD
	%			%		
Sand	68.1	55.6–80.6	2.8	71.6	51.5–89.2	5.0
Silt	18.9	10.0–26.8	5.0	16.1	5.0–27.8	7.7
Clay	13.0	7.2–17.6	8.4	12.3	5.8–20.8	13.2

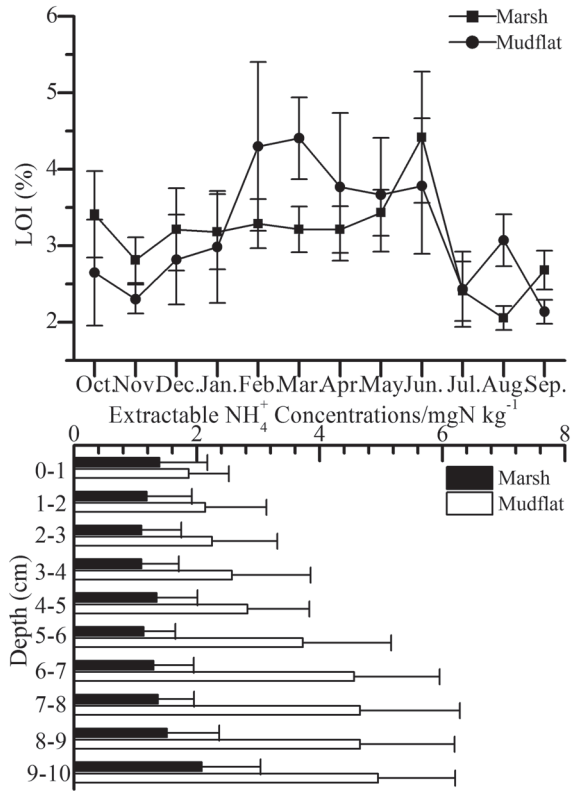

Fig. 4. Mean loss on ignition (LOI) of sediment cores (error bars represent SEM; *n* = 10) and extractable ammonium (NH_4^+) concentrations in sediment at marsh and mudflat sites (error bars represent SD; *n* = 12).

Discussion

Seasonal Change of Physicochemical Properties of Surface Water and Sediment

In winter, lower rates of N mineralization and nitrification in sediment and water as well as the lower temperatures overall likely led to higher DO in surface waters (Chai et al., 2006; Wang et al., 2007). Flooding controls the salinity in Yangtze estuary. In summer, fresh water enters into the estuary, and the prevailing south wind can carry this water into the Chongming mudflat and marsh area, leading to decreased salinity. In winter, the Yangtze River discharge is less, and seawater intrudes into the Yangtze estuary (Pan and Shen, 2010). At the same time, the prevailing north winds push seawater into the estuary, and the salinity increases in winter as a result.

The finding that NO_3^- was the main component of DIN in the surface water in the Chongming tidal flat is similar to what is seen with Mississippi River water discharging into estuarine and coastal waters of the southern United States (Bargu et al., 2011; Roy and White, 2012). The seasonal patterns of nutrient concentrations in surface water at the Chongming tidal flat and marsh areas have been previously reported (Chai et al., 2006; Pan and Shen, 2010). Higher temperatures in summer can promote greater biogeochemical cycling, and in particular higher nitrification and denitrification rates, which we surmised led to lower NO_3^- and NH_4^+ concentrations (Liu et al., 2009; Pan and Shen, 2010). In addition, NH_4^+ can be influenced by ions in sea water such that increases in salinity in surface water could induce desorption of NH_4^+ from the sediment via ion exchange (Rysgaard et al., 1999). This mechanism is likely the reason that NH_4^+ concentrations were positively correlated with salinity in surface water. It has been reported that the variations of NO_2^- concentrations in Yangtze estuarine water were primarily affected by the discharge of the Yangtze River (Li et al., 2007; Pan and Shen, 2010). This observation has been further confirmed in this study by the significant negative correlation between the NO_2^- concentrations and salinity of surface water.

Sediment characteristics can vary with topography, especially for measures of particle size and organic matter content (Malvarez et al., 2001; Yang et al., 2008). At the marsh site, there was vegetative growth that could potentially trap fine-grained sediment (Yang et al., 2008), whereas the mudflat was barren of macrophytes. Consequently, there is a greater chance that more fine particles will be deposited at the marsh site due to trapping than at the mudflat site. Winter storm activity led to erosion of the surface of the tidal mud flat site, resulting in wide fluctuations in values of soil carbon over the year (Chen et al., 2005a). Vertical patterns in extractable NH_4^+ concentrations in sediments at Chongming tidal flat were consistent with data reported in the literature (Malecki et al., 2004; Gardner and White, 2010). The presence of vegetation may alter the reduction environment of marsh sediment due to the transportation of oxygen to the rhizosphere; thus, nitrification may be promoted, resulting in decreased NH_4^+ concentrations in marsh sediment. Additionally, NH_4^+ concentrations can be depleted in soil through uptake by macrophytes (VanZomeren et al., 2012, 2013).

Seasonal Change of Dissolved Inorganic Nitrogen Fluxes

The diffusion of NH_4^+ from sediment into the surface water at the marsh in July, August, and October was expected because the anaerobic wetland soils are generally a large source of NH_4^+ (Hou et al., 2005; White and Reddy, 2000). Given the high ambient NO_3^- concentration, it is likely that the NH_4^+ in surface waters is consumed by nitrification and algal uptake. The wide annual variability of DIN flux rates underscores the need for intensive sampling over time to more accurately characterize estuarine sediment N flux dynamics.

Concentrations in surface water have been reported to affect sediment–water exchanges of dissolved species in estuaries (Cook et al., 2004; Gao et al., 2009). In our study, however, no significant correlations were observed between DIN fluxes and surface water nutrient concentrations, except for the significant positive correlation between NH_4^+ flux rates and surface water concentrations at the mudflat site and significant negative correlations for NO_2^- flux and surface water concentration at the marsh site (Table 3). Therefore, in this system, it is likely that variability in DIN fluxes might be governed by environmental and ecosystem factors, such as changes in the overlying water characteristics (e.g., pH, DO, salinity, and temperature) and microbial activity, as opposed to solely the N concentrations in the surface water. In our study, only NH_4^+ flux rates at the marsh site were positively correlated with water temperature and negatively correlated with salinity and DO (Table 3). The weak correlations between nutrient fluxes and environmental factors have been demonstrated by other researchers (Sakamaki et al., 2006; Wang et al., 2007). This result suggests that N flux rates might be influenced more by a complex suite of environmental factors.

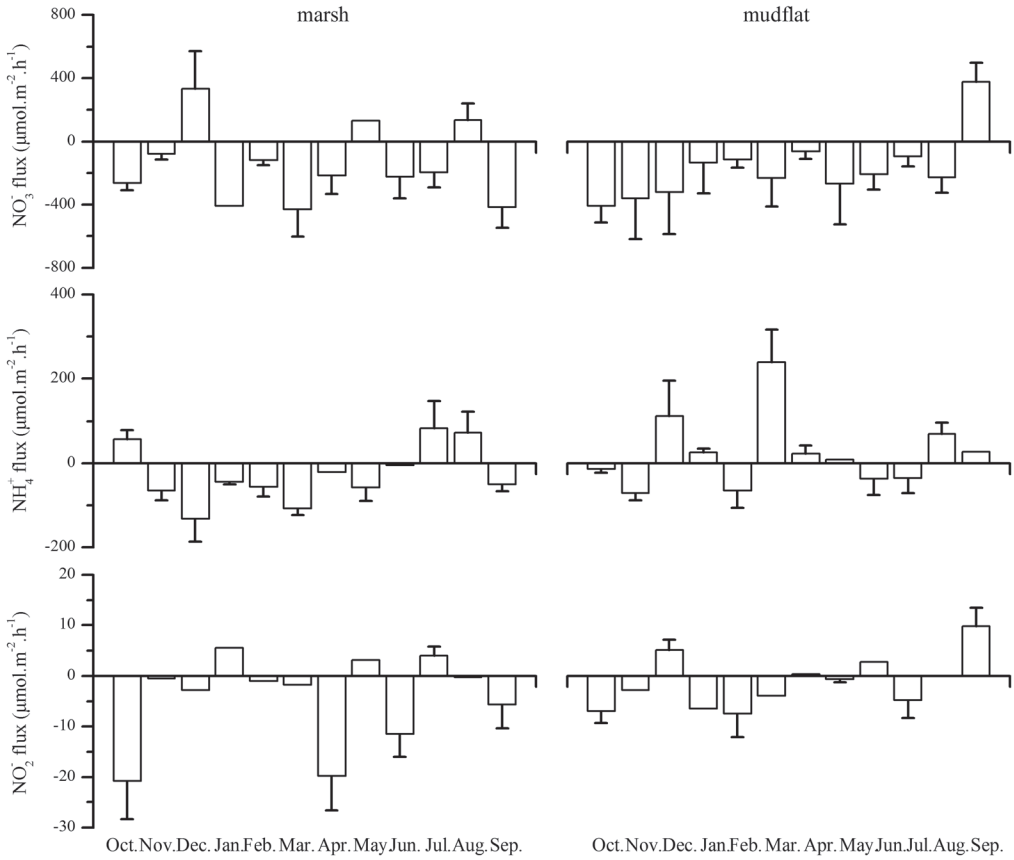

Fig. 5. Nitrite (NO_2^-), nitrate (NO_3^-), and ammonium (NH_4^+) fluxes across the sediment–water interface at marsh and mudflat sites. Positive fluxes indicate direction from sediment to the water column (error bars represent SD; *n* = 3).

The sediment–water interface is an active digenetic zone where a diverse heterotrophic microbial community is actively involved in mineralization and other nutrient transformations (Sun and Wakeham, 1998). Nitrogen cycling processes can include immobilization, mineralization/ammonification, nitrification, dissimilatory NO_3^- reduction to NH_4^+, and denitrification. These processes can affect exchanges of DIN at the sediment–water interface (Herbert, 1999; Wang et al., 2007; Koop-Jakobsen and Giblin, 2009). The NO_3^- flux rates accounted for the majority of the DIN flux rates; therefore, the behavior of NO_3^- determined the overall DIN flux. Nitrate can be removed primarily through two microbial pathways: denitrification and dissimilatory NO_3^- reduction to NH_4^+. Wang et al. (2006) reported that the sediment denitrification rate in the eastern portion of Chongming Island ranged from 1.12 to 33.34 μmol N m^{-2} h^{-1}. However, this denitrification rate accounts for only a small portion of the NO_3^- removal in our study. Therefore, dissimilatory NO_3^- reduction to NH_4^+ might be another transformation pathway for NO_3^-, as well as uptake by macrophytes at the marsh site.

Comparison of Laboratory Incubation versus In Situ Dissolved Inorganic Nitrogen Flux Rates

Feuillet-Girard et al. (1992) reported that differences in sampling methodology can account for discrepancies between fluxes determined in the laboratory compared with those measured in the field, whereas others have found no significant differences (Rabouille et al., 2003; Sundbäck et al., 2003). We compared the field flux rates from this study with our previously published research on DIN flux rates at the marsh and mudflat determined by laboratory incubation (Chen et al., 2005b; Deng et al., 2013). In the laboratory, intact sediment cores were

Table 3. Pearson correlation coefficients between dissolved inorganic nitrogen flux rates and water quality parameters of surface water (*n* = 12).

Site	Fluxes	NO_2^-	NO_3^-	NH_4^+	Temperature	Salinity	Dissolved oxygen
		μmol L^{-1}			°C	‰	mg L^{-1}
Marsh	NO_3^-	–0.279	–0.365	0.086	0.083	0.071	–0.041
	NH_4^+	0.457	–0.094	–0.572	0.771**	–0.752**	–0.682*
	NO_2^-	–0.737**	–0.510	0.169	0.042	0.194	0.088
Mudflat	NO_3^-	0.312	–0.097	–0.185	0.252	–0.376	–0.243
	NH_4^+	–0.039	0.027	0.818**	–0.315	0.480	0.155
	NO_2^-	0.441	–0.131	0.120	0.216	–0.194	–0.378

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

incubated in the dark in controlled temperature conditions. The overlying water in each sediment core was mixed and aerated by using an air pump (Chen et al., 2005b; Deng et al., 2013), similar to the in situ method. One difference from the laboratory study is that the in situ apparatus was exposed to sunlight. However, high suspended sediments in the surface water likely prevented light from penetrating far into the water column. In addition, the cells of the field study were covered by black netting, which was used to fix the entire apparatus in place, likely minimizing any effect of light. The results showed that there were no significant differences ($p > 0.05$) between NO_3^- fluxes measured in situ (-158.4 ± 218.2 μmol m^{-2} h^{-1}) and in laboratory incubations (-117.5 ± 337.9 μmol m^{-2} h^{-1}), but NH_4^+ flux rates in situ (-2.13 ± 80.3 μmol m^{-2} h^{-1}) were significant lower than in laboratory incubations (-188.6 ± 222.5 μmol m^{-2} h^{-1}; $p < 0.05$), although there were higher concentration of NO_3^- and NH_4^+ in surface water of the laboratory incubation than in our in situ research. Therefore, laboratory flux rates appear to sufficiently describe DIN dynamics during the time periods when NO_3^- dominates the DIN pool in this system. However, when NH_4^+ makes up a greater portion of the DIN pool, it is possible that field rates may be more appropriate. Laboratory incubations generally homogenize temperature throughout the soil column and remove macrophyte influences as well as the lateral subsurface movement of water and nutrients, which can modify flux rates.

Conclusion

Extractable NH_4^+ concentrations were significantly higher at depth at the mudflat site than at the marsh site, likely due to plant uptake at the marsh sites. The NO_3^- fluxes across the sediment–water interface occupied the major portion (55–97%) of total DIN fluxes, and NO_2^- fluxes were insignificant compared with NO_3^- and NH_4^+ fluxes. Over the year, mudflat sediment and marsh soil at Chongming Island served as a sink of DIN from the surface water (mudflat, -164.9 μmol m^{-2} h^{-1}; marsh, -177.7 μmol m^{-2} h^{-1}). In general, there were no significant correlations between DIN fluxes and single environmental factors, including temperature, salinity, or DO of the water column. Therefore, we conclude that DIN fluxes are likely controlled by a combination of DIN concentrations, sediment properties (e.g., organic matter, particle size, etc.), and parameters of overlying water (e.g., temperature, pH, DO, salinity, etc.). In situ total DIN fluxes were not significantly different from reported rates from laboratory incubations; however, in situ NH_4^+ flux rates were significantly lower than laboratory incubations, suggesting environmental–biotic controls on NH_4^+ flux in the field.

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