Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries

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Abstract

We conducted continuous-flow experiments on intact sediment cores from Laguna Madre, Sabine Lake, East Matagorda Bay, and Nueces Estuary to evaluate internal nitrogen (N) sources, sinks, and retention mechanisms in Texas estuaries having different salinities. Mean ammonium (NH_4^+) flux ranged from slight uptake (negative values) to NH_4^+ production rates of about 300 μmol m^{-2} h^{-1} (units used for all N rates) and increased with salinity ($p = 0.10$). Net nitrate (NO_3^-) flux (-20 to 32) and net N_2 flux (-70 to 100) did not relate to salinity. Mean net N_2 flux was positive but near zero, indicating that N_2 sources and sinks are nearly balanced. Total denitrification, N fixation, and potential dissimilatory NO_3^- reduction to NH_4^+ (DNRA) rates were estimated after inflow water was enriched with $^{15}NO_3^-$ (100 μmol L^{-1}). Total denitrification rates ranged from 0 to 90 versus N fixation rates ranging from 0 to 97. Potential DNRA, measured conservatively as $^{15}NH_4^+$ accumulation, ranged from 0 to 80 and related significantly to salinity ($p < 0.01$). Increases in total NH_4^+ release after $^{15}NO_3^-$ additions were higher but closely related ($r = 0.9998$) to $^{15}NH_4^+$ accumulation, implying exchange reactions of DNRA-regenerated $^{15}NH_4^+$ with sediment-bound $^{14}NH_4^+$. The fate of NO_3^- was related to salinity, perhaps via sulfide effects on DNRA. Potential DNRA was high in southeastern Corpus Christi Bay in August during hypoxia when the sulfide transition zone was near the sediment surface. Nitrogen fixation and DNRA are important mechanisms that add and retain available N in Texas estuaries.

Nitrogen (N), a key nutrient limiting primary production in coastal ecosystems, can be introduced to coastal waters via tributaries, atmospheric deposition, or groundwater inputs as nitrates (NO_3^- or NO_2^-), ammonium (NH_4^+), and organic N, or through N-fixation (Brock 2001; Paerl et al. 2002; Seitzinger et al. 2002). Available N is removed from coastal waters via physical transport, sediment burial, or conversion to gaseous forms, such as N_2 or N_2O, via denitrification (Seitzinger et al. 1984; Brock 2001). An improved understanding of N dynamics in coastal systems is needed to predict the effects of nutrient inputs from various sources and how input reductions may affect ecosystem dynamics (Pennock et al. 1999; Twilley et al. 1999).

Primary and secondary production in coastal ecosystems often depend on internal N cycling in the water column or sediments. Coastal sediments provide a matrix for processes affecting sources, transformations, and sinks of N (Blackburn and Sørensen 1988; Twilley et al. 1999). For example, redox gradients in sediments are conducive to denitrification, an N sink (Seitzinger 1988), or dissimilatory nitrate reduction to ammonium (DNRA), which keeps available N in the system as NH_4^+ (Rysgaard et al. 1996; An and Gardner 2002). DNRA differs from assimilatory reduction of NO_3^- to NH_4^+, which occurs via planktonic food web processes, in that it requires reduced conditions with an electron donor, such as sulfide, and does not involve an organic N intermediate.

Texas coastal systems include shallow estuaries, bays, and lagoons of varying salinities ranging from fresh in river mouths to hypersaline (>36) in the Laguna Madre (Solis and Powell 1999). Freshwater inflow is a major issue in south Texas because of limited and variable inflows and multiple demands for freshwater (Montagna and Kalke 1992). Nitrogen is the most limiting nutrient in these waters (Pennock et al. 1999; Brock 2001). Nitrogen sources and fates are important components for conceptual and mathematical models describing nutrient and food web dynamics. Such models help managers recognize and evaluate remedial ac-
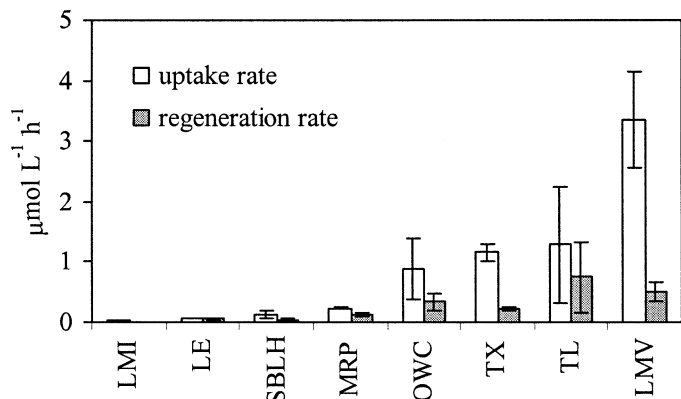
Fig. 1. Comparison of NH_4^+ uptake and regeneration rates determined from isotope dilution bottle experiments in various locations. LMI = Lake Michigan (Gardner et al. 2004); LE = Lake Erie; SBLH = Saginaw Bay, Lake Huron (Gardner et al. 1995b); MRP = Mississippi River Plume (Gardner et al. 1997); OWC = Old Woman Creek, a hypereutrophic tributary of Lake Erie; TX = Texas estuaries; TL = Taihu Lake, a hypereutrophic lake in China; LMV = Lake Maracaibo, a hypereutrophic lake in Venezuela (Gardner et al. 1998). Data from LE, OWC, TX, and TL have not yet been published. Note the large range bars (SE) at some sites (e.g., TL and OWC) reflect large trophic gradients among samples rather than analytical variation.
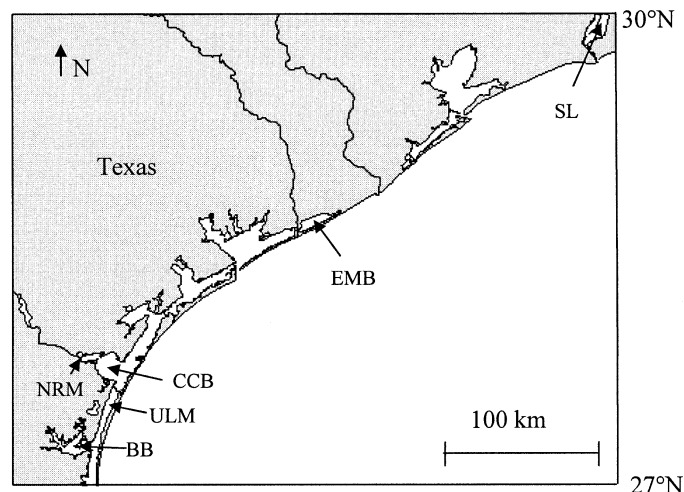

Fig. 2. Map of Texas estuaries and sampling regions. SL = Sabine Lake, EMB = East Matagorda Bay, CCB = Corpus Christi Bay, NRM = Nueces River Mouth, ULM = upper Laguna Madre, BB = Baffin Bay.

tions needed to improve water quality (e.g., Christian and Thomas 2003) or assess implications of system changes on fisheries productivity (e.g., Mortazavi et al. 2000; Brock 2001) or other regional and global issues (Boyer and Howarth 2002).

Published and unpublished data obtained with similar methods (Fig. 1) suggest that N-cycling rates in Texas coastal waters are comparable to rates observed in hypereutrophic ecosystems such as Lake Maracaibo (Venezuela), Taihu Lake (China), and Old Woman Creek (tributary of Lake Erie), and higher than rates observed in the Mississippi River plume in the northern Gulf of Mexico and the Great Lakes. This result is not intuitive because tributary nutrient inputs are limited in arid coastal regions in south Texas. A recent summary of Gulf of Mexico estuarine benthic processes (Twilley et al. 1999) indicated that benthic fluxes of dissolved inorganic N compounds also are not sufficient to support observed primary production rates. An important question is: "What is the N source supporting high productivity and N cycling rates observed in these coastal ecosystems, which are often N limited?" Atmospheric N_2 fixation may be a major source of available N in these systems. For example, algal mats at the sediment–water interface are active regions for fixation and may provide N, which can be recycled in the system (Paerl and Zehr 2000). Although biological N fixation is important to the N cycle at regional and global scales, it has been not included or underrepresented in most ecological models (Vitousek et. al. 2002). Nitrogen fixation has not been studied thoroughly in Texas estuaries, but rates exceeded those of denitrification when examined in Laguna Madre (An et al. 2001). This process should be considered in conjunction with denitrification and other internal processes to evaluate its relative importance.

Nitrogen transformations and fate may relate to salinity in coastal ecosystems. A higher percentage of mineralized N is denitrified at the sediment–water interface in freshwater than in marine systems (Seitzinger 1988). Potential mechanisms include salinity-driven increases in NH_4^+ fluxes out of the sediments due to ion pairing of NH_4^+ with salt water anions (Gardner et al. 1991) and blocking of ion exchange sites by seawater cations (Seitzinger et al. 1991); inhibition of nitrification/denitrification by sulfide (Joye and Hollibaugh 1995); and effects on microorganism physiology (Rysgaard et al. 1999). DNRA is enhanced by sulfide- or sulfate-reducing bacteria (Rysgaard et al. 1996) and occurs in coastal regions (Sørensen 1978; Tobias et al. 2001), including the Laguna Madre (An and Gardner 2002).

In this paper, N flux and transformation processes are examined seasonally along the Texas coast, ranging from low-salinity river mouths and brackish Sabine Lake to the hypersaline Laguna Madre/Baffin Bay. Specific questions addressed are: (1) What are the relative rates of sediment N-transformation processes in Texas estuaries? (2) Do N transformations at the sediment–water interface reflect net fixation (source) or net denitrification (sink) for available N? (3) How do DNRA and other sediment–water N transformation rates and fluxes relate to salinity and redox conditions in these dynamic systems?

Site descriptions—The Texas coast (Fig. 2) is subtropical and characterized by shallow bays and lagoons with a substantial rainfall gradient from northeast to southwest along the coast (Solis and Powell 1999). Mean annual rainfall ranges from >140 cm at the Texas–Louisiana border to about 65 cm in the arid southern regions, where evaporation exceeds rainfall and causes high salinities in enclosed regions, such as the Laguna Madre. This range in rainfall and salinities makes the Texas coast a "natural laboratory" to investigate river input and salinity effects on N dynamics (sources, fluxes, transformations, and fate) in coastal environments. Most waters in the area are oxic because of wind

mixing and shallow depths, but hypoxia occurs in southeastern Corpus Christi Bay and other areas where water residence times are long (about 5.5 months; Montagna and Kalke 1992; Ritter and Montagna 1999).

Laguna Madre Estuary (Fig. 2) is located south of Corpus Christi. It is the largest (by area) and longest of any Texas estuary and separated from the Gulf of Mexico by Padre Island. No major rivers or streams discharge into this system (Orlando et al. 1993). Upper Laguna Madre and Baffin Bay have a water residence time of about 1 yr and freshwater input is, on average, less than evaporation. About 65% of total freshwater discharged into the estuary is from direct precipitation (Orlando et al. 1993). Salinities are often >40 and can reach up to 60 (Buskey et al. 1998). Laguna Madre has been affected by Texas brown tide, a nuisance algal bloom persisting more than a decade (Buskey et al. 1998). The Texas brown tide organism, *Aureomonas lagunensis*, can use NH_4^+ or NO_2^-, but not NO_3^-, as an N source (DeYoe and Suttle 1994).

Sabine Lake is a shallow, brackish (mean salinity about 10) lake/tidal lagoon about 22.5 km long and 11.3 km wide. It is formed by the confluence of the Neches and Sabine Rivers, located on the Louisiana–Texas boundary, and drains about 130,000 km² of Texas and Louisiana into the Gulf of Mexico.

East Matagorda Bay is located between Matagorda and Galveston Bays (Fig. 2) and has little direct freshwater inflow except rainfall. Part of the Colorado River flows directly to the Gulf of Mexico, and its delta separates Matagorda and East Matagorda Bays. East Matagorda Bay is oriented in a southwest–northeast direction for about 32 km and has a width of about 6.5 km. It is enclosed on all sides with indirect access to small tributaries via the Gulf Intracoastal Waterway and with the Gulf of Mexico via Mitchell's Cut, which is sometimes closed, at the northern end of the bay (Kraus and Militello 1999). Few studies have focused on this shallow (maximum depth <2 m), muddy bay, except for a survey of freshwater inflow effects on macrobenthos abundance (Montagna 2001).

The Nueces Estuary is a shallow, microtidal estuary near Corpus Christi (Fig. 2). It includes Corpus Christi Bay (average depth 3.6 m) and two secondary bays (Nueces Bay and Oso Bay), which average 2 m and 1 m in depth, respectively. The estuary is separated from the Gulf of Mexico by a barrier island and has exchange with the Gulf via Aransas Pass, a restricted inlet. The drainage basin is semi-arid but, like the other regions, subjected to occasional tropical storms and flood flows (Brock 2001). Sediment–water nutrient fluxes and denitrification rates were measured for this estuary and compared to results from the Guadalupe Estuary (Yoon and Benner 1992; Twilley et al. 1999), but N fixation was not measured. Indirect evidence suggested that DNRA may be important (Yoon and Benner 1992).

Methods

Continuous-flow experiments to quantify nutrient and gas fluxes were conducted on intact sediment cores after each sampling event. Characteristics of continuous-flow methodology have been described and compared to closed-system approaches (Kana et al. 1994; Miller-Way and Twilley 1996; An et al. 2001).

Bottom water at each station was collected for nutrient analysis and sediment core incubations. Undisturbed sediment cores (7.6 cm inner diameter, ca. 30 cm length; three per station) were collected from a boat using a coring device equipped with a polyvinyl chloride pipe handle and a one-way rubber valve (bathroom flush valve) to preserve core and overlying water integrity. After transport to the laboratory, an adjustable flow-through plunger with O-ring seal and Teflon inlet and outlet tubes was installed over each sediment core (Lavrentyev et al. 2000; An et al. 2001). Each continuous-flow chamber consisted of an intake water vessel, Teflon flow tubes, a peristaltic pump, temperature-controlled incubation bath, and sample-collection vessels. Water column depth over the sediment was maintained at about 5 cm to give a water volume of about 230 ml over each core. Sediment cores were placed in the incubation bath at in situ temperature, and bottom water from the site was passed continuously over the core surface at 1.2 ml min⁻¹. The bottom water was aerated, except for experiments from Corpus Christi Bay hypoxic sites in August 2002, to maintain oxic conditions. Cores were wrapped with aluminum foil to prevent light effects, except for one half of the cores from Laguna Madre/Baffin Bay and Sabine Lake, which were incubated in dim light. After 1 d of incubation to achieve steady state, triplicate inflow and outflow samples were collected once or twice daily for dissolved gas analysis by membrane inlet mass spectrometry (MIMS). Dissolved N_2, O_2, and Ar were measured with MIMS using methods (An et al. 2001) modified from Kana et al. (1994). Additional samples were collected for analysis of dissolved inorganic N (DIN) compounds. Nitrate and NO_2^- were analyzed with a Lachat QuikChem 8000 FIA, and NH_4^+ concentration and isotopic content were measured by high-performance liquid chromatography (HPLC; Gardner et al. 1995a). Sediment flux was calculated for each compound on the basis of the concentration difference between inflow and outflow water, flow rate, and cross-sectional area (Lavrentyev et al. 2000).

Isotopic enrichment experiments were conducted to provide information needed to estimate N fixation, total denitrification, and DNRA rates (An et al. 2001). Inflow water was enriched with $^{15}NO_3^-$ (about 100 μL^{-1} final concentration) after the second sampling day. Three different masses of N_2 gas produced by denitrification were measured using MIMS ($^{28}N_2$ from $^{14}NO_3^-$, $30N_2$ from $^{15}NO_3^-$, and $^{29}N_2$ from $^{14}NO_3^-$ and $^{15}NO_3^-$; An et al. 2001). Concentration and atom% ^{15}N-NH_4^+ were determined by HPLC (Gardner et al. 1995a). Nitrogen fixation and potential DNRA rates were calculated as described in An et al. (2001) and An and Gardner (2002), respectively. These extended experiments with $^{15}NO_3^-$ additions (An et al. 2001) were done on all cores except Laguna Madre in April and August 1999.

An additional $^{15}NH_4^+$ experiment was done on East Matagorda Bay sediments to examine uptake and release exchange of NH_4^+ at the sediment–water interface under conditions otherwise similar to the $^{15}NO_3^-$ addition experiments. Triplicate cores were collected, set up, and equilibrated as described above. Twenty micromoles per liter $^{15}NH_4^+$ plus

100 μmol L^{-1} $^{14}NO_3^-$ were added to the inflow water and measurements were conducted as described. Total NH_4^+ uptake was calculated by measuring $^{15}NH_4^+$ uptake (as the decrease of $^{15}NH_4^+$ in the outflow vs. the inflow water) and dividing it by the $^{15}NH_4^+$: total NH_4^+ ratio in the outflow water. Total NH_4^+ release was calculated as the difference between net NH_4^+ flux and total NH_4^+ uptake.

Sediment cores for microelectrode analysis were taken from Corpus Christi Bay during seasonal hypoxia in August 2002 and during norm-oxic conditions in April 2003. Cores were collected manually by SCUBA divers with care to minimize disturbance during collection, covered and clasped with fitted tops, and taken to the laboratory. Vertical (i.e., downcore) measurement steps were every 1 mm for the first 10 mm, then every 2 mm to 60 mm, and every 5 mm to 100 mm. Porewater O_2 and $\Sigma H_2 S$ were measured simultaneously by anodic stripping voltammetry using solid-state potentiometric microelectrodes (Luther et al. 1998). Electroanalytical techniques were linear sweep and cyclic voltammetry, which was applied to the potential range from -0.1 V to 2.1 V. Calibration of each electrode was based on the pilot ion method where Mn was the standardized ion (Brendel and Luther 1995).

Results

Physical and chemical characteristics of sampling sites— Physical and chemical data for the different experimental sites are presented in Table 1. Water depths ranged from 0.4 to 2.2 m at most stations but were 2.7 to 3.0 m at the southeastern Corpus Christi Bay sites. Water temperatures ranged from 11°C in the winter to 30°C in summer. Near-bottom oxygen levels ranged from about 3 to 8 mg L^{-1} except for southeastern Corpus Christi Bay sites in August and one site in Baffin Bay, which had concentrations ranging from 0.1 to 2.3 mg L^{-1}. Ammonium, NO_3^-, and NO_2^- concentrations were low (<0.1 to 3 μmol L^{-1}) at most sites but sometimes higher (Table 1). Major exceptions were one Baffin Bay site in April 1999 with an NH_4^+ concentration of 17 μmol L^{-1} and the Nueces River Mouth site in July 2001 with a NO_3^- concentration of 67 μmol L^{-1} (Table 1).

Nitrogen dynamics.—Measured nitrogen fluxes and transformation rates for the various systems are shown in Tables 2–5. Each value is a mean (in μmol m^{-2} h^{-1}) from replicate cores ($n = 2$–3). Positive rates indicate net concentration increases, whereas negative values reflect removal from the water. Before $^{15}NO_3^-$ addition, NH_4^+ flux ranged from -31 to 231, with a mean of 60 ± 10 (SE), versus ranges and means of -20 to 32 and 3.2 ± 1.3, for NO_3^-, and -5.0 to 10.6 and 1.7 ± 0.5, for NO_2^-. Net N_2 flux ranged from -154 (net N fixation) to 530 (net denitrification) with a mean of 19 ± 16. Total N fixation, measured after $^{15}NO_3^-$ addition, ranged from 0 to 97 and had a mean of 32 ± 6 versus a range of 4 to 70 and mean of 32 ± 3 for total denitrification measured as N_2. Note that these values do not include Laguna Madre Estuary results from April 1999 and August 1999, which had highest values for net denitrification, because $^{15}NO_3^-$ enrichment experiments were not done on cores from those sampling dates.

Interesting differences among stations were observed in how the $^{15}NO_3^-$ additions affected the fluxes of total NH_4^+ and $^{15}NH_4^+$ in the cores. In the Laguna Madre Estuary, mean NH_4^+ flux increased to 262 ± 81 for the samples analyzed after $^{15}NO_3^-$ addition versus 87 ± 16 for the same samples before additions. Measured DNRA (i.e., $^{15}NH_4^+$ accumulation from the added $^{15}NO_3^-$) ranged from 16 to 51 with a mean of 41 ± 13 and accounted for only 23% of the mean difference (175) in NH_4^+ flux before and after $^{15}NO_3^-$ addition in this region. Thus, the increase in total NH_4^+ flux after $^{15}NO_3^-$ addition was about fourfold higher than accounted for by the measured DNRA for the same group of samples. By contrast, NH_4^+ fluxes after $^{15}NO_3^-$ enrichment (27 ± 20) were not distinguishable from those before addition (35 ± 23) in Sabine Lake, where DNRA rates were low. Likewise, NO_3^- flux was not different before and after $^{15}NO_3^-$ addition in the lake. Mean fluxes overlapped with zero in both cases. Potential DNRA in Sabine Lake ranged from -1 to 5.5, mean 0.9 ± 0.8, versus a range and mean of -66 to 68 and 16 ± 16 for total denitrification (Table 3). In East Matagorda Bay, mean NH_4^+ flux after $^{15}NO_3^-$ addition, 40 ± 5, was higher than the mean value of 23 ± 5 before the addition. Nitrogen fixation, 3 ± 2, and $^{15}NH_4^+$ accumulation from DNRA, 3.6 ± 0.6, were low relative to denitrification, 22 ± 4, after the addition (Table 4). Overall, N dynamics at these intermediate salinity stations were between values of Sabine Lake and the hypersaline Laguna Madre waters. In contrast to other sites, mean NO_2^- flux, an indicator of active N dynamics, was more than half of that for NO_3^- at East Matagorda Bay sites.

Results of the $^{15}NH_4^+$ addition experiment conducted on East Matagorda Bay cores (Fig. 3) indicate that, although the initial net NH_4^+ flux was positive, it represented steady-state equilibrium of exchange reactions between the water column and sediments. The addition of $^{15}NH_4^+$ interrupted steady-state conditions and caused net flux of total NH_4^+ to be -88 the first day after addition, but it decreased to -15 on the second day. Thus, total NH_4^+ uptake (171 to 279) and release (83 to 216) rates, calculated after the $^{15}NH_4^+$ isotope addition, were much greater than the measured net NH_4^+ fluxes before or after the isotope addition. Note that the calculated total NH_4^+ uptake and release demonstrate active exchange, but the measured net flux is more important ecologically because it represents the active flux of NH_4^+ beyond steady-state sediment–water exchange.

The Nueces River Mouth site, sampled only in July 2001 at salinity 0.29, had a positive NH_4^+ flux of about 40, but NO_3^- and NO_2^- fluxes were near zero (Table 5), even though NO_3^- concentration was high in the overlying water (Table 1). Net N fixation occurred at that station, and N fixation rates, after $^{15}NO_3^-$ enrichment, were more than twice as high as denitrification rates (Table 5). DNRA rates were low but measurable. The upper Corpus Christi Bay site, sampled only in July 2001 at salinity 2.0, had minimal N fluxes before $^{15}NO_3^-$ addition. Positive NH_4^+ flux and measurable denitrification and DNRA rates, but no N fixation, were observed after the addition (Table 5).

The three southeastern Corpus Christi Bay sites, where hypoxia is common (Ritter and Montagna 1999), provided an opportunity to observe N-transformation differences under similar salinities but different redox conditions. Seasonal

Table 1. Physical and chemical characteristics of the water at experimental sites in Laguna Madre (L), Baffin Bay (B), Sabine Lake (SL), East Matagorda Bay (EMB), Nueces River mouth (NRM), and Corpus Christi Bay (CCB).

Station	Date	Depth (m)	Temp (°C)	Salinity	DO (mg L^{-1})	NH_4^+ (μmol L^{-1})	NO_3^- (μmol L^{-1})	NO_2^- (μmol L^{-1})
L155	Apr 99	0.73	26.9	32.8	6.39	0.2	0.6	0.2
	Aug 99	0.56	30.2	38.1	5.32	0.4	<0.03	<0.03
	Dec 99	0.61	15.6	32.1	5.88	<0.1	0.2	0.4
	Apr 00	1.33	20.5	34.3	6.65	<0.1	8.9	1.1
L189	Apr 99	0.44	26.4	31.1	6.35	0.2	0.7	0.1
	Aug 99	0.74	29.6	37.3	4.53	<0.1	0.4	0.2
	Dec 99	0.60	15.8	31.4	6.33	<0.1	0.2	0.4
	Apr 00	1.45	20.8	34.3	6.61	<0.1	8.8	1.1
B6	Apr 99	2.07	26.2	23.3	4.37	16.8	3.4	1.1
	Aug 99	2.22	30.8	19.2	1.35	<0.1	0.4	0.3
	Dec 99	1.75	16.2	30.5	7.09	<0.1	<0.03	0.3
	Apr 00	2.20	26.1	26.6	5.76	<0.1	1.7	1.1
B24	Apr 99	1.69	26.0	21.1	5.87	0.2	0.8	<0.03
	Aug 99	1.75	30.4	24.1	6.90	<0.1	0.3	0.3
	Dec 99	1.66	15.8	25.7	5.61	<0.1	<0.03	0.3
	Apr 00	1.80	25.9	25.0	5.73	<0.1	1.8	1.0
SL1	Jun 00	2.20	29.5	7.9	5.44	0.7	1.4	<0.03
	Sep 00	2.00	28.5	15.2	5.30	0.6	1.1	<0.03
	Dec 00	2.06	10.6	4.8	7.63	5.3	5.4	0.4
	Mar 01	2.17	16.4	0.5	5.95	<0.1	2.0	0.9
SL2	Jun 00	1.79	29.4	6.3	3.01	0.6	1.4	<0.03
	Dec 00	1.42	12.4	4.1	6.60	5.7	7.5	0.4
	Mar 01	2.03	15.8	0.1	6.41	<0.1	2.5	0.9
EMB-A	Jun 01	1.24	29.1	17.9	4.65	<0.1	0.3	0.2
	Jul 01	1.45	29.5	22.2	3.67	2.4	2.1	0.2
	Oct 01	1.57	23.1	17.1	4.79	<0.1	1.6	0.3
	Jan 02	1.37	14.3	15.1	5.69	<0.1	1.3	0.4
	Apr 02		23.0	25.0		<0.1	2.2	0.4
	Jul 02	1.67	30.4	29.5	5.98	1.5	0.5	<0.03
EMB-F	Jun 01	1.01	29.5	19.6	4.90	<0.1	0.1	0.1
	Jul 01	0.88	30.2	27.7	3.70	1.6	2.7	0.2
	Oct 01	1.16	23.6	18.5	4.70	<0.1	1.8	0.2
	Jan 02	1.03	14.5	21.9	5.54	<0.1	1.7	0.4
	Apr 02		23.0	25.5		<0.1	3.3	0.3
	Jul 02	1.18	30.4	24.3	6.05	1.2	1.1	0.1
NRM	Jul 01	0.88	30.0	0.3	4.61	1.4	66.7	<0.03
CCB	Jul 01	1.05	32.3	2.0	13.3	0.8	2.0	0.03
CCB-24	Aug 02	2.70	30.2	27.6	0.11	<0.1	0.9	<0.03
	Apr 03	2.70	21.9	28.4	3.56	0.4	0.5	0.1
CCB-12	Aug 02	2.70	29.6	24.5	2.32	1.4	1.1	<0.03
	Apr 03	2.70	21.8	28.7	6.15	0.2	0.8	0.2
CCB-10	Aug 02	3.00	29.9	26.3	0.52	<0.1	0.8	<0.03
	Apr 03	3.00	21.8	28.7	6.14	<0.1	0.6	0.1

differences in redox conditions, NH_4^+ regeneration, N fixation, and DNRA rates were observed for cores sampled in August 2002 and April 2003 (Table 5). Oxygen levels in overlying water were 0.98 ± 0.68 mg L^{-1} in August and 5.3 ± 0.9 mg L^{-1} in April (Table 1). Oxygen and sulfide transition zones were nearer to the sediment surface in August than in April (Fig. 4). Corresponding NH_4^+ fluxes were 86 ± 24 in August versus 2.9 ± 4.0 in April. Nitrate and NO_2^- fluxes (respective means of 0.7 ± 1.4 and 0.5 ± 0.1) were much lower than NH_4^+ fluxes and did not show predictable patterns with season. Net N_2 flux indicated net denitrification in August (31 ± 4) but net N fixation in April (-65 ± 7). Total N-fixation rates were low in August (2.7

± 2.7) but higher in April (30 ± 7). Denitrification rates were moderately, but not significantly, higher in August (52 ± 15) than in April (40 ± 5). DNRA rates were about six times higher in August (22 ± 6), when oxygen levels were low, than in April (3.6 ± 1.1) under norm-oxic conditions (Table 5). In contrast to results from other sites where DNRA was observed, significant increases in total NH_4^+ release after the $^{15}NO_3^-$ enrichment were not observed in August. Moderate increases in NH_4^+ release after enrichment were observed in April.

Possible linear relationships between respective fluxes and salinity were examined for sites having overlying water O_2 concentrations >3 mg L^{-1}. Corpus Christi Bay data from

Table 2. Seasonal rates of sediment N transformations or fluxes in Laguna Madre and Baffin Bay (μmol N m^{-2} h^{-1}).

Station	Date	NH$_4^+$†	NH$_4^+$*	NO$_3^-$†	NO$_2^-$†	Net N$_2$†	NF*	DNRA*	DNF*
L155	Apr 99	26		−1.7	1.7	200			
	Aug 99	56				54			
	Dec 99	59	161	0.4	0.6	−28	76	51	47
	Apr 00	25	98	1.8	−1.2	8	56	16	19
L189	Apr 99	187		2.0	0.2	530			
	Aug 99	60		0.1	0.7	28			
	Dec 99	128	638	0.7	0.7	−16	51	99	46
	Apr 00	128	302	1.1	0.8	−6	64	32	22
B6	Apr 99	151		−3.7	5.9	180			
	Aug 99	231		−0.5	1.1	82			
	Dec 99	84	146	0.7	0.6	36	58	18	24
	Apr 00	215		−0.4	−1.1	−18			
B24	Apr 99	151		32.3	10.6	118			
	Aug 99	131		1.9	−0.5	36			
	Dec 99	115	230	1.2	0.8	20	44	29	34
	Apr 00	6		−0.4	0.1	−24			
Mean		110	262	2.4	1.4	73	58	41	32
SE		17	81	2.2	0.8	31	5	13	5

† Values measured before ^{15}NO$_3^-$ addition (100 μmol L^{-1}) to inflow water. NF, N fixation; DNRA, dissimilatory NO$_3^-$ reduction to NH$_4^+$; DNF, total denitrification. (See Also An and Gardner 2002 where data were first reported.)

* Values measured after isotope addition.

August 1999 were not included to prevent the salinity comparison from being biased by reducing conditions. Mean NH$_4^+$ flux before ^{15}NO$_3^-$ enrichment increased with salinity ($p = 0.10$). Likewise, DNRA rates were related ($p < 0.01$) to salinity (Fig. 5). However, net NO$_3^-$ and N$_2$ fluxes and total denitrification (calculated after ^{15}NO$_3^-$ addition) showed no pattern with salinity.

Discussion

Seasonal and regional rates of sediment N transformations along the Texas coast—Results from experiments in Texas coastal systems show that N transformations were dynamic at the sediment–water interface but varied spatially and temporally in relative importance and magnitude (Tables 2–5). The most active processes, in terms of net flux magnitude, were NH$_4^+$ production from the sediments, N fixation, and denitrification. Reactions involving NO$_3^-$ and NO$_2^-$ may have been dynamic, but their concentrations and net changes

remained low during most experiments, indicating that they were static or in steady-state equilibrium. Mean sediment NH$_4^+$ fluxes before and after isotope additions were positive or near zero at all sites except Sabine Lake in December 2000, which showed net NH$_4^+$ uptake. Observed NH$_4^+$ accumulation and measurement of potential DNRA rates suggest that DNRA was a major component of total NH$_4^+$ production at some stations.

Benthic nutrient fluxes in nine Gulf of Mexico estuaries have been examined by several investigators and reviewed (Twilley et al. 1999). In agreement with results from other Gulf of Mexico estuaries (Yoon and Benner 1992; Zimmerman and Benner 1994; Twilley et al. 1999), mean NH$_4^+$ sediment regeneration rates (net fluxes) in the present study ranged from about 20 to 110 μmol m^{-2} h^{-1}. Results for NO$_3^-$ fluxes also follow patterns similar to previous results (Yoon and Benner 1992; Zimmerman and Benner 1994) in Texas estuaries, except for Guadalupe Estuary, which exhibited high NH$_4^+$ uptake (~150 μmol m^{-2} h^{-1}) and NO$_3^-$ (plus

Table 3. Seasonal rates of sediment N transformations in Sabine Lake (μmol N m^{-2} h^{-1}). See Table 2 for column definitions.

Station	Date	NH$_4^+$†	NH$_4^+$*	NO$_3^-$†	NO$_2^-$†	Net N$_2$†	NF*	DNRA*	DNF*
SL1	Jun 00	68.2	46.4	7.4	1.2	−30.4	97.0	1.1	31.4
	Sep 00	145	123	5.7	3.4	89.8	80.2	5.5	67.9
	Dec 00	−30.9	−31.9	15.1	0.7	−37.2	41.4	0.0	48.2
	Mar 01	6.7	−3.8	0.4	−0.5	−25.7	12.1	0.1	22.2
SL2	Jun 00	13.1	11.1	1.8	0.4	−77.4		0.8	
	Dec 00	−19.9	−10.5	−20.4	−1.0	−39.8	56.3	0.0	3.9
	Mar 01	60.5	51.9	−0.5	−5.0	−56.1	10.9	−1.1	6.8
Mean		34.7	26.6	1.4	−0.11	−25.3	49.7	0.91	30.1
SE		23.1	19.7	4.1	0.97	20.3	14.4	0.81	10.1

Table 4. Seasonal rates of sediment N transformations or fluxes in East Matagorda Bay (μmol N m^{-2} h^{-1}). See Table 2 for column definitions. Note that N fixation and denitrification data were not recovered after $^{15}NO_3^-$ addition for sites sampled in June, July, and October 2001 because of a data collection malfunction.

Station	Date	NH$_4^+$†	NH$_4^+$*	NO$_3^-$†	NO$_2^-$†	Net N$_2$†	NF*	DNRA*	DNF*
EMB-A	Jun 01	30.5	38.4	13.9	5.3	−154		1.6	
	Jul 01	0.0	58.8	1.3	2.4	−18.4		4.6	
	Oct 01	13.3	29.8	5.9	−0.9	106		5.4	
	Jan 02	0.6	−2.9	−2.6	−0.7	−29.6	0.0	2.3	12.1
	Apr 02	30.9	60.8	4.3	1.3	7.0	0.0	6.0	23.2
	Jul 02	27.8	40.0	27.4	7.1	−6.2	4.2	5.4	28.7
EMB-F	Jun 01	32.4	51.4	6.7	8.0	−31.5		0.4	
	Jul 01	0.0	29.8	4.3	3.3	−16.0		2.0	
	Oct 01	48.6	62.1	2.3	3.0	73.4		6.9	
	Jan 02	29.9	22.8	8.0	2.7	−30.0	0.0	2.3	17.3
	Apr 02	19.8	47.1	3.3	4.0	1.5	0.0	2.6	13.6
	Jul 02	44.6	45.7	11.7	10.7	−21.0	12.6	4.1	40.3
Mean		23.2	40.3	7.2	3.9	−9.9	2.8	3.6	22.5
SE		4.8	5.4	2.2	1.0	18.1	2.1	0.6	4.4

NO$_2^-$) release rates (~175 μmol m^{-2} h^{-1}; Twilley et al. 1999). However, this observation may have been an exception to normal conditions as another study showed only moderate DIN fluxes in Guadalupe Estuary (Yoon and Benner 1992). Large spatial and temporal variations in N fluxes within and among estuaries make it difficult to discern patterns among them. For example, nutrient fluxes in Laguna Madre were lowest among estuaries examined in the earlier comparison (Twilley et al. 1999) but highest in the present comparison. The predominance of Texas brown tide in the 1990s may have affected this comparison. Dense populations of *A. lagunensis* remove NH$_4^+$ from solution and keep concentrations low in the water (Gardner unpubl. data).

Sediment–atmosphere interactions: Is the sediment–water interface a site of net N$_2$ fixation (source) or net denitrification (sink) for available N?—Two approaches were taken to evaluate N fixation versus denitrification. First, net N$_2$ flux before $^{15}NO_3^-$ addition indicated whether atmospheric N$_2$ was a net source (N fixation) or sink (denitrification) of available N at the sediment–water interface. However, net changes do not reveal the extent to which N fixation and denitrification occur simultaneously. The isotope pairing approach (An et al. 2001) allows estimation of total rates for each process in

the same cores but may not portray "actual rates" if the processes are affected by $^{15}NO_3^-$ addition.

In contrast to NH$_4^+$ fluxes, which were almost always positive, net N$_2$ fluxes ranged from positive to negative values seasonally at the same sites and regionally among the sites. In Laguna Madre, net denitrification occurred on five occasions, net N fixation occurred twice, and zero net exchange occurred once. The opposite was observed in Sabine Lake, with N fixation dominating on six of seven occasions. In East Matagorda Bay, net N fixation was observed on 8 of 12 sampling occasions, but net rates were sometimes close to zero. Overall, net fixation was observed in the summer and winter (dry seasons) and net denitrification was observed in the spring and fall (wet seasons). Nitrogen fixation (Table 5) dominated in southeastern Corpus Christi Bay during April when O$_2$ levels were high in overlying waters (Fig. 4). However, denitrification dominated (Table 5) during summer when bottom water O$_2$ levels were low and the sulfide transition zone was near the sediment surface (Fig. 4). DNRA was six times higher at these sites in August than in April.

Net N$_2$ flux results from all stations indicated that mean changes were low but slightly positive (19 ± 16 μmol m^{-2} h^{-1}), indicating that the two processes were nearly balanced

Table 5. Seasonal rates of sediment N transformations or fluxes at Nueces Estuary sites (μmol N m^{-2} h^{-1}). See Table 2 for column definitions.

| Station	Date	NH$_4^+$†	NH$_4^+$*	NO$_3^-$†	NO$_2^-$†	Net N$_2$†	NF*	DNRA*	DNF*
NRM	Jul 01	42.4	40.7	−1.0	1.3	−17.6	54.6	3.2	21.2
CCB	Jul 01	0.0	77.0	−1.3	0.1	10.1	0.0	2.6	24.9
CCB-24	Aug 02	53.1	65.4	3.4	0.3	38.7	0.0	31.3	69.8
	Apr 03	−2.1	27.0	0.6	0.8	−76.8	36.8	4.3	49.8
CCB-12	Aug 02	72.4	63.3	−4.9	0.4	31.2	0.0	9.9	62.8
	Apr 03	−1.6	1.7	−1.2	0.8	−65.0	36.8	1.4	33.4
CCB-10	Aug 02	133	141	4.1	0.2	24.2	8.2	24.8	23.0
	Apr 03	12.5	28.2	2.2	0.5	−53.8	16.6	5.0	35.4
Mean		38.7	55.5	0.2	0.5	−13.6	19.1	10.3	40.0
SE		16.8	15.0	1.0	0.1	16.4	7.4	4.0	6.6
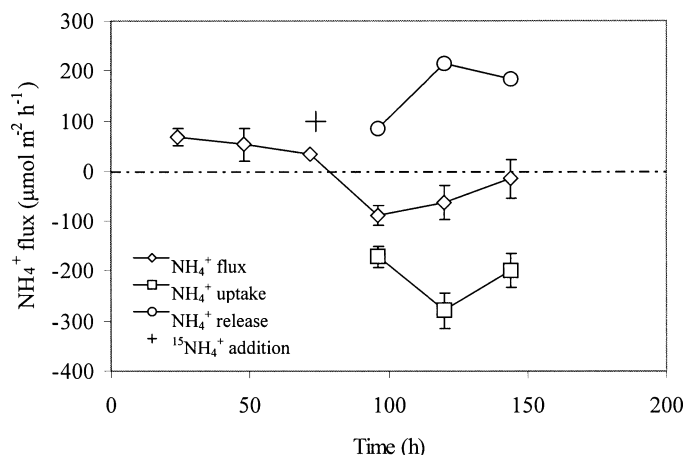
Fig. 3. Net and total NH_4^+ uptake and release in East Matagorda Bay sediments after addition of $^{15}NH_4^+$. Positive values indicate flux from the sediments to the water, whereas negative values indicate removal from the water.

across the region. Denitrification rates from the present study were similar but, on average, higher than previous closed-chamber results in Texas estuaries (Yoon and Benner 1992; Zimmerman and Benner 1994). Underwater chamber results from Galveston Bay (An and Joye 2001) yielded higher denitrification rates than the present study and demonstrated that denitrification rates were higher in the light (mean N = 1000 μmol m^{-2} h^{-1}) than in the dark (mean N = 480 μmol m^{-2} h^{-1}).

Total N fixation versus denitrification rates, calculated in the enriched cores with the MIMS isotope pairing method, indicated that both processes proceeded simultaneously at comparable but different rates. For example, in Laguna Madre, mean postenrichment rates were 58 ± 5 for N fixation, 32 ± 5 for denitrification, and 41 ± 13 for DNRA. Net N$_2$ flux was 2.3 ± 9.7 for the same cores before enrichment (excluding cores where enrichment experiments were not done). Unfortunately, $^{15}NO_3^-$ enrichments were not performed in April and August 1999 when highest net denitrification rates occurred. When these cores are included, net denitrification was dominant because of a large temporal effect. Results for both processes may be conservative since measurements did not account for N$_2$O production via incomplete denitrification. Also, both processes may be higher in natural light than dark or dim-light incubations because of labile organic matter production by photosynthesis (An and Joye 2001; An and Gardner 2002). Nitrogen fixation in Laguna Madre may have been underestimated since seagrasses were not included in experimental cores. Previous studies indicate that N fixation rates are high in seagrass beds where organic material is abundant (Paerl and Zehr 2000).

Data from the present study suggest that N fixation and denitrification are important and provide critical supply and removal mechanisms for available N in these productive systems. Although they occurred in both directions, net N$_2$ fluxes across the sediment–water interface were comparable to NH_4^+ fluxes and much higher than net NO_3^- or NO_2^- fluxes. This active exchange between atmospheric N$_2$ and biotic N helps explain why Texas coastal systems have sufficient N
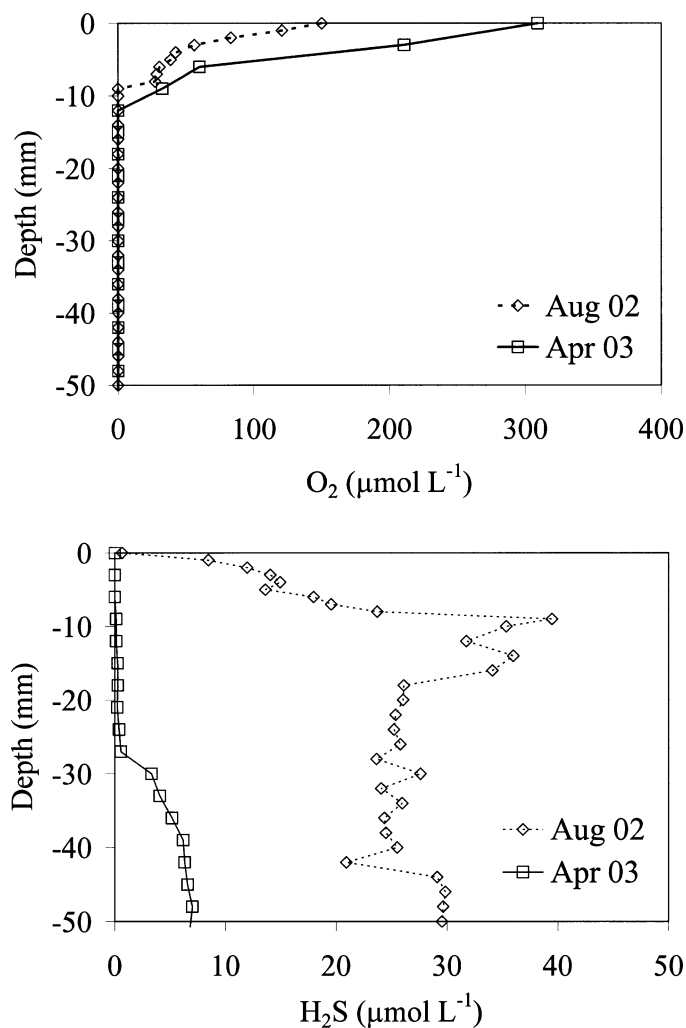

Fig. 4. Mean sediment–depth gradients for O$_2$ and H$_2$S for three stations in southeastern Corpus Christi Bay in August 2002 and April 2003.
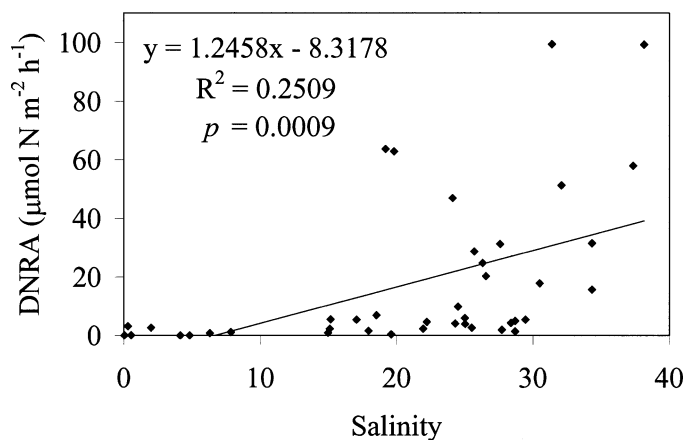

Fig. 5. Relationship of DNRA rates to salinity for stations represented in Tables 2–5.

inputs to support high water-column N cycling rates, comparable to those in hypereutrophic ecosystems (Fig. 1), despite limited tributary nutrient inputs.

Relationship of DNRA to salinity and evidence for displacement of sediment-bound NH_4^+ by DNRA-produced NH_4^+—Measuring N dynamics in sediment cores from a range of salinities provided an opportunity to examine relationships between N transformations and salinity and how they affect N removal or retention. Ammonium flux and DNRA rates increased with increasing salinity, but none of the other processes showed a significant salinity relationship. Denitrification:DNRA decreased significantly ($p < 0.01$) with increasing salinity, suggesting that the fate of NO_3^- in surface sediments is related to salinity via DNRA and that DNRA is an important mechanism for retaining N in a biologically available form under saline conditions. DNRA also has been reported in other coastal systems (Koike and Hattori 1978; Sørensen 1978; Tobias et al. 2001). Enhancement of DNRA by sulfide- or sulfate-reducing bacteria (Rysgaard et al. 1996) is consistent (1) with the observed significant relationship between DNRA rates and salinity (with sulfate as a source) and (2) the large increase in DNRA rates observed when high sulfide concentrations, associated with low O_2, occurred near the sediment–water interface in Corpus Christi Bay (Fig. 4). The production of NH_4^+ by DNRA under conditions of high salinity may help explain why the Texas brown tide organism, *A. lagunensis*, which requires reduced N compounds as an N source, has thrived in the Laguna Madre Estuary when salinities were high (An and Gardner 2002). *Aureoumbra lagunensis* density in the estuary correlated directly with salinity at three stations sampled from July 1997 through October 1998 (Buskey et al. 2001).

Changes in total NH_4^+ release after $^{15}NO_3^-$ enrichment were proportional to but greater ($r = 0.9998$, $a = -12.3$, $b = 7.41$, $p < 0.01$) than DNRA rates when mean rates from Laguna Madre, Sabine Lake, and East Matagorda Bay were compared. These results imply that $^{15}NO_3^-$ enrichment may affect total NH_4^+ production, presumably via DNRA. The slope of this relationship indicates that increased NH_4^+ release stimulated by NO_3^- enrichment was about seven times the $^{15}NH_4^+$ accumulation fraction on average. However, this relationship did not hold if Corpus Christi Bay data were included, particularly in August 2002 when higher DNRA rates appeared to relate to reducing conditions rather than salinity.

Observed differences between the increases in total NH_4^+ release after enrichment versus $^{15}NH_4^+$ accumulation at normoxic stations indicates that rates estimated from the latter measurement may have underestimated potential DNRA. The $^{15}NH_4^+$ produced from $^{15}NO_3^-$ via DNRA may have exchanged with sediment-bound $^{14}NH_4^+$ (Rosenfeld 1979; Gardner et al. 1991; Seitzinger et al. 1991) as it diffused or migrated from the redox transition zone, where DNRA would occur, through the sediment to overlying water. If such exchange occurred, some $^{15}NH_4^+$ would have displaced $^{14}NH_4^+$ on sediment exchange sites and resulted in increased $^{14}NH_4^+$ release from the sediments. This exchange would cause the measurement of released $^{15}NH_4^+$ in the overflowing water to underestimate potential DNRA resulting from the

$^{15}NO_3^-$ enrichment when there is a zone of oxygenated sediments above the redox transition zone. The active exchange of NH_4^+ between the water and sediments, observed in the $^{15}NH_4^+$ addition experiment on East Matagorda Bay cores (Fig. 3), illustrates why increases in total NH_4^+ release were greater than $^{15}NH_4^+$ accumulation after $^{15}NO_3^-$ addition.

The migration distance to the overlying water for NH_4^+ formed from DNRA would be minimized where the water is hypoxic and the redox transition zone is at or near the sediment surface (e.g., August 2002, Corpus Christi Bay). This temporal difference in redox transition depth is illustrated by comparing mean O_2 and sulfide profiles for Corpus Christi Bay stations sampled in August 2002 versus April 2003 (Fig. 4). The mean transition depth was ~1 mm in August versus 28 mm in April. In agreement with this concept, there was no evidence for $^{15}NH_4^+ : ^{14}NH_4^+$ isotope exchange reactions in the core experiments from August 2002 (i.e., mean total NH_4^+ release showed a slight decrease despite the presence of measurable $^{15}NH_4^+$; Table 5). However, mean total NH_4^+ release increased after $^{15}NO_3^-$ enrichment in April 2003 (Table 5) when O_2 and sulfide transition zones were deeper (Fig. 4).

Exchange reactions between free and bound NH_4^+ explain why measured $^{15}NH_4^+$ in outflow waters accounted for only a fraction of NO_3^- removal in isotope-addition experiments (An and Gardner 2002). A second possible sink for removed $^{15}NO_3^-$, which was not converted to $^{15}NH_4^+$, is incomplete denitrification to N_2O and subsequent loss to the atmosphere (Smith et al. 1983). However, previous studies indicate that N_2O produced in estuarine sediments is small relative to N_2 (e.g., Seitzinger et al. 1983).

Evaluation of sediment–water N fluxes and transformations in Texas coastal systems offers insights about mechanisms controlling the sources and fate of available N in shallow, productive systems with variable and limited N inputs. Spatial and temporal similarities and differences in these processes among sites and seasons provides information about dominant cycling mechanisms and the importance of atmospheric N_2 as a source or sink for available N. The observed simultaneous N fixation and denitrification rates are consistent with the concept that available N compounds exchange actively with atmospheric N_2 and that N fixation is an important N source. Measurements of both processes were conservative since denitrification rates did not include N_2O production and assessments were not made under natural light or in the presence of seagrasses, conditions that would enhance production of labile organic compounds, which could serve as an energy source for N-transformation processes.

The observed relationship between sediment NH_4^+ release and salinity suggests that NH_4^+ regeneration increases with salinity. DNRA is an important process contributing to that trend. DNRA increased with salinity and was most important in Laguna Madre. DNRA also was important in southeastern Corpus Christi Bay during seasonal hypoxia. Comparison of potential DNRA rates estimated from $^{15}NH_4^+$ accumulation with those estimated from increased total NH_4^+ fluxes after $^{15}NO_3^-$ enrichment suggest that $^{15}NH_4^+$ accumulation can underestimate potential DNRA in sediments under oxygenated waters.

Overall, our results are consistent with the concepts that N fixation is important in Texas estuaries and that DNRA helps retain available N in hypersaline estuaries. They help explain why N cycling rates in Laguna Madre and other Texas estuaries resemble those for hypereutrophic systems even though tributary inputs are limited.

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