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Andrew R. Zimmerman
University of Texas at Austin

Ronald Benner
University of South Carolina - Columbia, benner@mailbox.sc.edu

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Denitrification, nutrient regeneration and carbon mineralization in sediments of Galveston Bay, Texas, USA

Andrew R. Zimmerman*, Ronald Benner**

Marine Science Institute, University of Texas at Austin, Port Aransas, Texas 78373, USA

ABSTRACT: Rates of benthic denitrification, oxygen consumption and nutrient regeneration were measured during winter, spring and summer in Galveston Bay (Texas, USA) sediments. Denitrification ranged from 0 to 47 $\mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ with maximal rates generally occurring in the summer and the upper estuary. Oxygen consumption rates ranged from 38 $\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ in the winter to 353 $\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ in the summer and were correlated with denitrification rates. Variations in bay water temperature accounted for 52 % of the variability associated with denitrification rates whereas only 28 % of the variability could be attributed to organic carbon content and 15 % to salinity, indicating a predominance of temporal over spatial factors in controlling estuarine rates of denitrification. In the spring and summer, denitrification was responsible for the majority (73 and 80 %, respectively) of the total benthic inorganic nitrogen efflux while in the winter, nitrogen fluxes were dominated (80 %) by ammonium. At salinities less than 6‰, cation exchange interactions may have played an important role in retaining ammonium in the sediment, producing the higher rates of denitrification found in the upper estuary. Dissolved inorganic carbon flux was used as a measure of total organic carbon mineralization. The average molar C:N of the remineralized substrate (5.2) was lower than the average C:N of the sediments (12.6) indicating preferential remineralization of nitrogen relative to carbon. Molar C:O ratios suggested that anaerobic carbon mineralization and the storage of its reduced end-products is more prevalent in the lower estuary and in the winter. Denitrifiers were responsible for 37 and 13 % of the total benthic carbon mineralization in the upper and lower estuary, respectively. Denitrification appears to be a greater contributor to total carbon mineralization than previously considered. Nearly one-third of the total sediment oxygen consumption was attributed to nitrification. Galveston Bay sediment denitrification and oxygen consumption rates and nutrient fluxes were lower but comparable to those of other Gulf of Mexico estuaries. Differences among the estuaries examined are attributed mainly to sediment organic matter content.

KEY WORDS: Denitrification · Galveston Bay · Benthic nutrient regeneration · Carbon remineralization · Nitrogen remineralization · Estuaries

INTRODUCTION

Benthic metabolism plays an important role in the regulation of nutrient concentrations and thus the productivity of estuarine and coastal marine systems. In the case of nitrogen, the main nutrient controlling the

productivity of estuaries (e.g. Nixon 1981, Boyton et al. 1982), sediments are a source as well as a major sink in the cycling of this element. The regeneration of ammonium in sediments is a major source of nitrogen to the water column, whereas production of dinitrogen gas (denitrification) and burial are major nitrogen sinks. Most of the organic matter reaching the sediments is microbially degraded, and the end products of microbial decomposition are largely influenced by the availability of various terminal electron acceptors. Estuaries serve as ideal systems in which to study these

*Present address: Virginia Institute of Marine Science, College of William and Mary, PO Box 1346, Gloucester Point, Virginia 23062, USA

**Addressee for correspondence

benthic processes as a gradient in the concentration of the most common terminal electron acceptors, molecular oxygen, nitrate and sulfate, exists naturally. Through a full accounting of the end products of these aerobic and anaerobic respirations, in both seasonal and spatial detail, we may gain an understanding of the role that sedimentary processes play in the cycling of bioactive elements within an estuary.

One objective of this study was to examine the factors which affect the rates of denitrification in estuarine sediments and the efficiency of this process in removing dissolved nitrogen from estuarine waters. Hundreds of measurements of estuarine denitrification rates have been made (reviews in Koike & Sørensen 1988, Seitzinger 1988), but many denitrification studies are not of great use for interestuary comparisons because of methodological differences, limited seasonal or spatial coverage, or a lack of background information on the amount or sources of nitrogen entering the estuary. It is also difficult to compare rates of microbial activity from estuaries of very different climate zones or sediment types. With the completion of this study, denitrification rates in 4 Gulf of Mexico estuaries have been made by the direct measurement of N_2 production. In each estuary, sediment oxygen consumption and the fluxes of dissolved inorganic nitrogen ($DIN = NO_3^-$, NO_2^- , NH_4^+) have also been recorded in both seasonal and spatial detail. Because there exists a gradient of decreasing salinity among Gulf coast estuaries from the southwest to the northeast, we were able to assess the influence of salinity on benthic NH_4^+ versus N_2 release. Gardner et al. (1991) proposed that NH_4^+ efflux is slowed by cation exchange interactions in freshwater systems. The increased sediment residence time of ammonium increases the opportunity for nitrification and denitrification to occur. Some interestuary comparisons are made which may shed light on the factors controlling denitrification rates and other benthic processes.

We also investigated the use of dissolved inorganic carbon (DIC) flux measurements as an integrative estimate of the total amount of carbon remineralized during benthic decomposition. Mackin & Swider (1989) and Sampou & Oviatt (1991) found that ΣCO_2 production measurements provide reliable estimates of the total integrated rate of organic carbon remineralization in coastal marine sediments. These investigators found that benthic metabolism was dominated by anaerobic processes in these systems. As a result, sedimentary oxygen consumption (SOC) was largely uncoupled from organic carbon oxidation by the temporally variable processes of storage and reoxidation of sedimentary sulfides. Greater carbon mineralization relative to SOC represented an excess of anaerobic relative to aerobic metabolism. Using this concept of

DIC and SOC balance we were able to examine the spatial and seasonal variability of these processes in Galveston Bay, Texas, USA. The suitability of this method is investigated as well as the use of the biological poisons formalin and mercury in sediment incubation chambers to distinguish chemical from biological sedimentary processes.

MATERIALS AND METHODS

Sampling sites. Five sampling sites were chosen in Galveston Bay as representative of the range of water salinities and organic carbon contents of sediments in the bay (Fig. 1). Sites 1 and 2 are located in Trinity Bay which receives 70% of the freshwater inflow to Galveston Bay from the Trinity River (NOAA 1989). Salinities at these sites remained below 3‰ during 1993 (Table 1), a year of slightly less than average salinities (TWDB & TPWD 1992). Sites 3 and 4 were established along the highly industrialized western shore of Galveston Bay. Site 3 is located at the entrance to Clear Lake and near the mouth of the San Jacinto River, both of which receive the outflow of many water treatment facilities. Site 4 is located in a basin just offshore from Texas City where there is a concentration of petroleum refineries. Site 5, and Site 6 in East Bay, are most closely in contact with seawater inflow from the Gulf of Mexico although water at both sites remained below 20‰ salinity and only slight vertical stratification of the water column was observed throughout the study period.

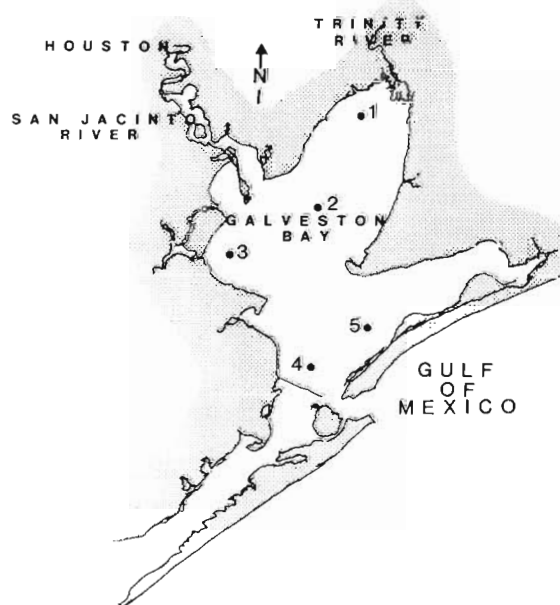


Fig. 1. Map of Galveston Bay, Texas, USA, with sampling sites

Table 1 Galveston Bay, Texas, USA, sampling sites and water temperatures, salinities and dissolved oxygen concentrations. Temperature and dissolved oxygen concentrations are for bottom water collected at each site. na: not available

Month	Station	Latitude	Longitude	Depth (m)	Temperature (°C)	Salinity (‰)		Dissolved O ₂ (mg l ⁻¹)
						Bottom	Surface	
March	1	29° 42' 06" N	94° 44' 38" W	2.1	15.0	na	0.0	na
	2	29° 37' 45" N	94° 49' 43" W	2.9	15.0	na	0.0	na
	3	29° 33' 22" N	94° 59' 44" W	2.8	17.5	na	4.0	na
	4	29° 22' 59" N	94° 50' 34" W	2.4	17.0	na	11.0	na
	5	29° 26' 27" N	94° 42' 54" W	1.8	17.5	na	10.0	na
May	1	29° 42' 06" N	94° 44' 38" W	2.1	22.4	0.2	0.2	8.3
	2	29° 37' 45" N	94° 49' 43" W	2.9	22.7	2.9	2.8	8.0
	3	29° 33' 22" N	94° 59' 44" W	2.8	23.1	5.8	5.8	7.5
	4	29° 22' 59" N	94° 50' 34" W	2.4	23.9	13.5	11.6	8.2
	5	29° 26' 27" N	94° 42' 54" W	1.8	24.1	11.7	10.5	7.5
July	1	29° 42' 06" N	94° 44' 38" W	2.1	29.5	0.2	0.2	7.0
	2	29° 37' 45" N	94° 49' 43" W	2.9	29.4	2.5	2.4	7.3
	3	29° 33' 22" N	94° 59' 44" W	2.8	29.8	4.8	3.0	5.2
	4	29° 22' 59" N	94° 50' 34" W	2.4	29.6	24.0	18.5	5.9
	5	29° 26' 27" N	94° 42' 54" W	1.8	30.3	7.7	5.7	5.1

Sediment collection and incubation. In early March, May and July of 1993, 6.7 cm i.d. cores were collected using a hand-held corer with removable acrylic liners. In addition, surface water samples were collected and vertical water-column profiles of temperature, salinity, pH and dissolved oxygen content were obtained using a Hydrolab Scout/H₂O system. The cores were transported at *in situ* temperatures ($\pm 4^\circ\text{C}$) to the Marine Science Institute in Port Aransas, Texas, and, within 24 h, the upper 7 cm of sediment was transferred with minimal disturbance into glass incubation chambers of the same inner diameter (Yoon & Benner 1992). Prefiltered (0.2 μm Nuclepore) bay water from each sampling site was added to each respective chamber so that a 65 ml gas volume remained above the overlying water. At the start of each incubation period, the chamber was sealed and purged for 1 h by sparging through the overlying water with a N₂-free gas mixture (21% O₂, 79% He). During an initial period of 9 d, the chambers were continuously shaken (65 rpm) and purged for 1 h each day to equilibrate dissolved gases and to allow the penetration of poison into sediments of the killed control chambers. This waiting period has been found to be sufficient for the rates of denitrification and nutrient exchange to become linear (Seitzinger et al. 1980, Yoon & Benner 1992). Subsequently, the chambers were continuously shaken (20 rpm) while incubated in the dark and at *in situ* temperatures.

Four replicate cores were collected at each site in Galveston Bay. One core was sectioned into 2 cm intervals and used to measure porosity (weighed before and after drying for 3 d at 60°C) and organic carbon

and total nitrogen content by flash combustion of HCl-acidified and dried samples using a Carlo Erba 1108 CHN analyzer. A second core was used to measure redox potential at 2 cm intervals with a platinum electrode (Orion Model 96-78). One core from each site was used to measure denitrification, total oxygen consumption, nutrient fluxes and carbon remineralization. A duplicate core was used as a killed control to monitor atmospheric contamination and chemical oxygen consumption rates. The killed control chambers were treated with 10 ml of formalin (37% formaldehyde) during the winter and spring sampling periods and 800 μl of saturated HgCl₂ solution during the summer incubations.

Details of the sediment incubation and gas sampling procedure and a discussion of the relative advantages and disadvantages of this method of denitrification measurement may be found in Yoon & Benner (1992). After gas sampling, 20 ml samples of water from the chambers were filtered (GF/F) and saved frozen in polypropylene vials for nutrient analysis and 20 ml samples were saved in gas-tight glass vials for DIC analysis. Chamber water was then replaced with new water from each site, sampled for initial nutrient and DIC measurements and resealed and sparged to begin the next incubation cycle. Periodic checks of initial concentrations of N₂, O₂ and DIC in each chamber's gas phase were made after sparging.

For each 2 to 3 d incubation period, fluxes were calculated as the difference in gaseous or aqueous concentrations of each species per unit time, per sediment surface area within the chambers. The average and standard deviation of 5 incubation periods for each core were calculated and reported. Based upon cal-

Table 3. Oxidation potential (Eh, in mV) of Galveston Bay sediments. na: not available

Depth (cm)	Site:	March					July				
		1	2	3	4	5	1	2	3	4	5
Surface		-19	-79	-279	4	-96	25	na	-20	-16	-230
1		-188	-262	-282	-242	-269	-69	na	-145	-205	-230
3		-248	-309	-296	-250	-270	-88	na	-255	-111	-270
5		-278	-328	-320	-261	-299	-110	na	-240	-284	-270
7		-330	na	-328	-288	-363	-144	na	-220	-260	-266

absolute terms, the average organic carbon content of the upper sediment layer also decreased from winter to spring to summer. These changes may be due to an increase in benthic processing of organic material in the upper sediment layers as temperatures increase. A corresponding winter to summer increase in organic C:N may be caused by the preferential degradation of nitrogen relative to carbon in the surface sediment and has been noted elsewhere (Aller & Yingst 1980, Blackburn & Henriksen 1983).

Denitrification, oxygen consumption and DIC production rates

The rates of denitrification in Galveston Bay sediments during the March sampling period were found to be low or not significantly different from zero at all sites except Site 1 (Table 4). Rates of oxygen consumption were also minimal during March ($<90 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$) at all sites except Site 1 ($452 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$).

Table 4. Denitrification (N_2 production), oxygen consumption and dissolved inorganic carbon (DIC) efflux from Galveston Bay sediments. Incubation temperatures were 16°C (March), 23°C (May) and 29.5°C (July)

Month	Site	N_2 production ($\mu\text{mol m}^{-2} \text{ h}^{-1}$)		O_2 consumption ($\mu\text{mol m}^{-2} \text{ h}^{-1}$)		DIC production ($\mu\text{g-at. C m}^{-2} \text{ h}^{-1}$)	
		Mean	SD	Mean	SD	Mean	SD
March	1	21	7	452	95	319	62
	2	0	4	38	45	32	26
	3	6	7	86	30	220	59
	4	0	2	64	75	258	46
	5	0	3	66	35	97	15
May	1	14	3	126	44	80	22
	2	35	9	224	85	186	24
	3	27	5	239	112	234	28
	4	0	5	63	47	131	31
	5	23	16	203	111	152	32
July	1	37	13	236	105	124	34
	2	47	16	286	107	237	26
	3	37	13	353	91	189	49
	4	10	6	230	121	121	31
	5	20	4	242	57	329	55

The Site 1 incubation chamber, however, contained a living bivalve (species *Macridae rangia*) of a body weight which could consume 20 to $200 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ through respiration (Dame 1972) and could account for the excess oxygen flux. The calculated respiratory quotient ($\text{RQ} = \Delta\text{CO}_2/\Delta\text{O}_2$) for chamber 1 is 0.7, similar to values commonly derived for aerobic respiration (Rich 1975). The increase in denitrification rate in this chamber could result from increased sediment irrigation bringing nitrate and nitrite in contact with anoxic regions of the sediment. Data from this incubation were excluded when examining trends in benthic processes.

Cores collected in May displayed higher denitrification rates (0 to $35 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$) and oxygen consumption rates ranging from 63 to $239 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$. After making these measurements, the chambers were purged with helium and the system was allowed to become anoxic and to exhaust all sources of nitrate. A mean nitrogen gas flux of $15.9 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ (SD = 6.8) was then recorded during 3 incubation periods, validating our use of $17.5 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ as a leakage rate and confirming the existence of a tight coupling between nitrification and denitrification. A mean DIC production value of $107 \mu\text{mol C m}^{-2} \text{ h}^{-1}$ was measured during the anoxic incubations, providing a rough estimate of the contribution of anaerobic processes (other than denitrification) to carbon mineralization during May.

Summer denitrification rates were the highest among the 3 sampling periods (10 to $47 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$) as were rates of oxygen consumption (230 to $353 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$). Excluding Site 5, where no increase in denitrification was measured, rates increased from a mean value of 19 to $33 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$, or nearly doubled from May to August while the temperature increased from 23 to 29.5°C. Although no simple link between denitrification rates and temperature can be drawn due to the possible effects of changes in other parameters such as redox conditions, nutrient availability and sediment irrigation, it is worth noting that this increase in denitrification from May to July would be equivalent to a Q_{10} (temperature coefficient = the rate increase for a tem-

perature increase of 10°C) of 2.1. During this same period oxygen consumption increased by 58% and carbon mineralization (DIC efflux) by 28%.

Although chambers with higher DIC production rates generally corresponded to those with higher oxygen consumption rates, a significant correlation between these 2 processes was not found. A molar equivalence of oxygen use and carbon dioxide production is predicted for aerobic respiration when ammonium is the final nitrogen-containing product of benthic mineralization of organic material. Further oxidation of ammonium to nitrate, for example, will drive the $\Delta\text{CO}_2/\Delta\text{O}_2$ ratio lower as will the chemical oxidation of reduced species stored in the sediment, such as pyrite. This ratio will be greater than 1 if the sediment is dominated by anaerobic processes and storage of its reduced end-products occurs. In Galveston Bay, nearly all the $\Delta\text{CO}_2/\Delta\text{O}_2$ ratios derived from upper-estuary site (Sites 1, 2 and 3) sediment incubations were 1 or less than 1 (mean = 0.96) indicating a predominance of aerobic heterotrophic activity or the absence of storage of reduced end-products of anaerobic metabolism (Fig. 2). In contrast, lower-estuary sediments consistently displayed much higher $\Delta\text{CO}_2/\Delta\text{O}_2$ ratios (mean = 1.7) and are therefore probably dominated by anaerobic carbon mineralization processes such as sulfate reduction. Storage of reduced metabolic products, of which sedimentary sulfide is probably the major form, seems to be of particular importance during the winter, while reoxidation of these species appears to occur primarily in the spring and summer. These trends may be linked to increased bioturbation during these warmer seasons. Caution ought to be exercised when interpreting these trends as both

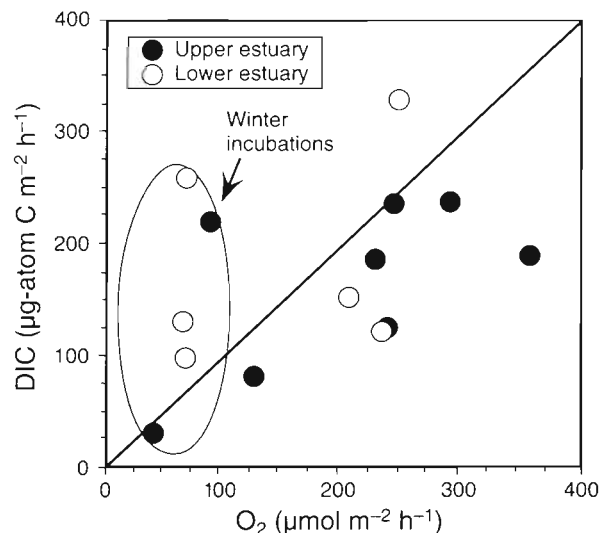


Fig. 2. Relationship between oxygen consumption and inorganic carbon production from upper (<6‰) and lower (>6‰) Galveston Bay sediments. Diagonal line: 1:1 molar between DIC and O_2 fluxes

anaerobic metabolism and chemical oxidation can and probably do occur concurrently. Fig. 2 is only indicative of likely sites or periods of predominance of one or another of these processes.

Benthic nutrient fluxes

The concentrations of phosphate, nitrate + nitrite (N+N) and ammonium in bay waters and the mean benthic fluxes of these species are listed in Table 5.

Table 5. Water concentrations and benthic fluxes of phosphate, nitrate and nitrite (N+N) and ammonium. Positive flux values are from the sediment into the overlying water and are the mean of fluxes measured during five 2 d incubation periods

Month	Site	Bay water nutrient concentrations (μM)			Benthic nutrient fluxes (μM m ⁻² h ⁻¹)					
		PO_4^{3-}	N+N	NH_4^+	PO_4^{3-}	SD	N+N	SD	NH_4^+	SD
March	1	0.8	39.9	5.0	3.5	1.1	-6.8	9.0	45.2	22.5
	2	1.6	32.9	1.1	-0.3	0.1	-10.1	0.9	3.1	2.3
	3	3.5	31.6	7.3	2.4	0.6	-12.3	2.8	18.2	5.6
	4	0.8	7.0	0.6	-0.6	0.3	-10.4	2.4	45.1	12.7
	5	0.3	0.3	0.5	-0.6	0.2	0.6	0.2	5.6	6.8
May	1	3.2	48.8	0.6	0.6	0.3	-17.2	1.2	0.4	0.6
	2	3.9	29.2	0.0	-1.1	0.5	-9.0	1.0	2.7	2.1
	3	3.6	1.2	1.1	-1.0	0.6	4.5	2.5	3.5	2.3
	4	2.4	5.3	2.1	0.3	0.1	-0.3	0.8	13.8	3.7
	5	1.9	1.1	1.8	0.0	0.2	7.9	5.1	4.1	4.1
July	1	2.9	15.6	1.2	3.1	0.6	-3.0	0.6	-0.2	0.3
	2	4.3	22.3	1.7	1.5	0.3	-7.2	1.2	0.6	0.9
	3	5.8	4.7	7.9	-2.6	0.5	3.0	2.9	-3.9	2.6
	4	2.5	0.9	6.1	2.4	0.8	12.7	3.6	7.6	6.4
	5	1.8	0.6	3.3	1.9	1.8	6.7	8.6	29.8	16.2

Bay water concentrations of N+N were always highest at upper-estuary sites and generally highest in the winter and spring due to their mainly riverine source. Trinity River gauged flow rates are usually highest from January to June (NOAA 1989). Bay water phosphate concentrations were highest in the summer and at Site 3 near the mouth of Clear Lake suggesting a benthic or anthropogenic source. Fluxes of phosphate between the sediment and overlying water were small ($<4 \mu\text{mol P m}^{-2} \text{ h}^{-1}$) but usually from the sediment to the water, particularly in the upper and mid-estuary and in the summer. These associations suggest that the observed phosphate fluxes result from the mineralization of organic matter. The diagenesis of iron oxyhydroxides at the redox boundary within the sediment also releases phosphate (Caraco et al. 1989), however, and may be another cause of the observed phosphate fluxes. The flux of N+N was generally from the water to the sediment at upper-estuary sites (-3 to $-17 \mu\text{g-at. N m}^{-2} \text{ h}^{-1}$) and from the sediment to the water at lower-estuary sites (0 to $13 \mu\text{g-at. N m}^{-2} \text{ h}^{-1}$). Influx of N+N predominated during the winter and spring while N+N efflux was of a greater magnitude during the summer. Ammonium fluxes (-4 to $45 \mu\text{mol NH}_4^+ \text{ m}^{-2} \text{ h}^{-1}$) were nearly always out of the sediment and were highest in the winter. These seasonal trends in NH_4^+ and N+N flux may be attributed to low rates of sedimentary nitrification in the winter relative to the summer.

Killed control experiments

During the winter and spring sampling periods, formalin was used to terminate all biological processes in the sediments of a core from each site. In previous studies (Dale 1978, Wang 1980, Barcelona 1983, Yoon & Benner 1992) biological oxygen consumption was calculated as the SOC of the live chambers (total O_2 consumption) minus that of the killed chambers (chemical O_2 consumption, mostly attributed to oxidation of sulfides and other reduced metallic phases). In the course of our experiments, however, SOC in the killed chambers was often greater than in the live chambers (winter mean: live 63 vs killed $130 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$; spring mean: live 52 vs killed $142 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$). Concurrent measurements of DIC effluxes in the killed chambers were 2 to 10 times that of the corresponding live chambers and decreases in pH (0.6 to 1.0 units) were also measured. These changes in pH, DIC and SOC were not observed when additional experiments were carried out under the same conditions but with overlying water of 30‰ salinity. We hypothesize that the addition of formalin to low salinity and therefore possibly less buffered waters caused a decrease in pH

and the dissolution of sedimentary carbonate. These chemical changes may have enhanced the exposure of reduced phases to chemical oxidation and produced the observed increases in O_2 consumption. Recent experiments with the use of formalin to distinguish chemical from biological oxygen consumption in sediments from Lake Vechten, The Netherlands, met with similar difficulties (Sweerts et al. 1991). The increased oxygen consumption of formalin-poisoned sediment was attributed to enhanced penetration of oxygen thus allowing the reduced products of anaerobic respiration to be oxidized.

The suitability of mercuric chloride (HgCl_2) for use as a poison in a sediment and water system was tested during the summer incubations. Drastic pH changes, high oxygen consumption and DIC production in the killed chambers were no longer observed but a mean flux rate of $28 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ was recorded instead of the expected $17.5 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ leakage rate. The formation of black sediment layers below the zone of oxidized surface sediment during the incubations suggested that sulfate reduction was still occurring and HgCl_2 was not an efficient poison. The effectiveness of HgCl_2 and formalin as biological poisons was investigated by adding ^{14}C -glucose to poisoned chambers and monitoring the production of $^{14}\text{CO}_2$. After 3 d of incubation, an average of 25% of the added glucose was recovered in the form of $^{14}\text{CO}_2$ from the HgCl_2 -killed chambers ($n = 5$) versus 1% in the formalin-killed chambers ($n = 5$). Clearly, HgCl_2 is not an effective poison for use in our system, probably due to the propensity of mercury to bind to sediments. Mercury is therefore unable to penetrate into deeper sedimentary layers and anaerobic microbial activity is able to continue. Formalin was an effective poison for stopping biological processes in sediments but the above-mentioned problems associated with carbonate dissolution and enhanced oxygen consumption preclude its use for estimation of biologically produced fluxes of these species.

Nitrogen inventory

By assembling an inventory of the measured fluxes of nitrogen species between the sediment and water (Table 6) some general characterizations of estuarine benthic exchanges can be made. First, it is clear that at no time in Galveston Bay could the measured influx of nitrate and nitrite to the sediment from the water fully support the measured rate of denitrification when significant denitrification did occur. This observation supports the now established doctrine that denitrification in sediments is strongly coupled to the process of nitrification as a provider of oxidized nitrogen species.

Table 6. Net and total nitrogen fluxes ($\mu\text{g-at. N m}^{-2} \text{ h}^{-1}$), calculated rates of nitrification ($\mu\text{g-at. N m}^{-2} \text{ h}^{-1}$), oxygen consumption by nitrification ($\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$), DIC production by denitrifiers ($\mu\text{g-at. C m}^{-2} \text{ h}^{-1}$) and the percentages of total O₂ consumption, N₂ production and DIC production supported by nitrification, N+N influx and denitrification, respectively

Month	Site	Net N flux ^a	Total N efflux ^b	Nitrification rate ^c	O ₂ consumption by nitrification ^d		N ₂ production supported by N+N influx	DIC production by denitrifiers ^e	
					Rate	%		Rate	%
March	1	80.8	87.6	36	72	16	16	53	17
	2	-7.0	3.1	0	0	0	0	0	0
	3	17.8	30.0	0	0	0	104	15	7
	4	34.6	45.0	0	0	0	0	0	0
	5	6.2	6.2	1	1	2	0	0	0
May	1	11.1	28.2	11	21	17	62	35	43
	2	63.2	72.1	61	121	54	13	87	47
	3	61.4	61.4	60	116	48	0	67	29
	4	14.4	14.6	0	1	1	42	1	1
	5	58.6	58.6	55	109	54	0	58	38
July	1	69.8	72.8	70	21	59	4	91	74
	2	87.1	94.4	87	121	61	8	117	49
	3	75.0	75.0	77	116	44	0	93	49
	4	40.3	40.3	33	1	28	0	25	21
	5	75.7	75.7	46	91	38	0	49	15
Annual averages									
Upper estuary		47	55	46	65	35	24	63	37
Lower estuary		38	40	22	34	21	7	22	13

^a Sum of dinitrogen, nitrate + nitrite (N+N) and ammonium fluxes. Positive values are from the sediment to the water
^b Sum of all N species (N+N, NH₄⁺, N₂) fluxes when out of the sediment only. Does not include dissolved organic nitrogen flux
^c Sum of N+N flux and the amount of N+N needed to supply the measured rate of denitrification. The stoichiometric ratio of 2 mol nitrate needed to produce 1 mol N₂ is used (Froelich et al. 1979)
^d Based on the overall reaction NH₄⁺ + 2 O₂ → HNO₃ + H₂O. Nitrite is considered as nitrate for the calculations
^e Calculated assuming 2.5 g-at. C used in the production of 1 mol N₂

Such was the conclusion of other denitrification studies carried out in estuarine (e.g. Seitzinger 1987, Yoon & Benner 1992) as well as coastal marine environments (e.g. Kaplan 1983, Devol & Christensen 1993). Other evidence of nitrification and denitrification coupling may be drawn from the strong positive correlation between measured rates of denitrification and oxygen consumption in all incubation chambers during all experiments ($r = 0.885$, $p < 0.001$).

In all cases except one, the sediment served as a net source of dissolved inorganic nitrogen to the overlying water. NH₄⁺ was the major component of the nitrogen flux during the winter while N₂ was the major component in the spring and summer. NH₄⁺ may be directly produced by the mineralization of organic material, but urea hydrolysis has also been found to be a major source of benthic NH₄⁺ (Lomstein et al. 1989). The highest rates of NH₄⁺ release were recorded during the winter incubations when concentrations of nitrate and nitrite in the water were also the greatest and the flux of nitrate into the sediment from the water was, on average, the highest measured. Very little denitrification was measured at this time. These observations suggest that dissimilatory NO₃⁻ reduction to NH₄⁺

may also be occurring at this time. Arguments both for (Koike & Hattori 1978, Sørensen 1978, Nishio et al. 1982, Jørgensen 1989, Cole 1990) and against (Binnerup et al. 1992) the existence of significant NO₃⁻ reduction to NH₄⁺ in estuarine sediment have been presented. If this process plays a significant role in nitrogen cycling in Galveston Bay, the estuary would be relieved, at least in part, of the nutrient sink represented by denitrification and possibly subject to a positive feedback mechanism causing increasing nutrient enrichment in bay waters at certain times of the year. Jørgensen & Sørensen (1985), examining sediments of a shallow estuary in Denmark, measured higher rates of NO₃⁻ reduction to NH₄⁺ in sediments nearer to the river mouth relative to those down-estuary and claimed this trend to be due to higher levels of NO₃⁻ in upper-estuary waters. We found a general correspondence, but no linear correlation, between water nutrient concentrations and benthic fluxes of N₂ or NH₄⁺.

The tendency for nitrogen to be released as NH₄⁺ rather than N₂ increases down-estuary (Fig. 3). It has been suggested that the diffusion of NH₄⁺ out of oxidized surface sediments is hindered in freshwater

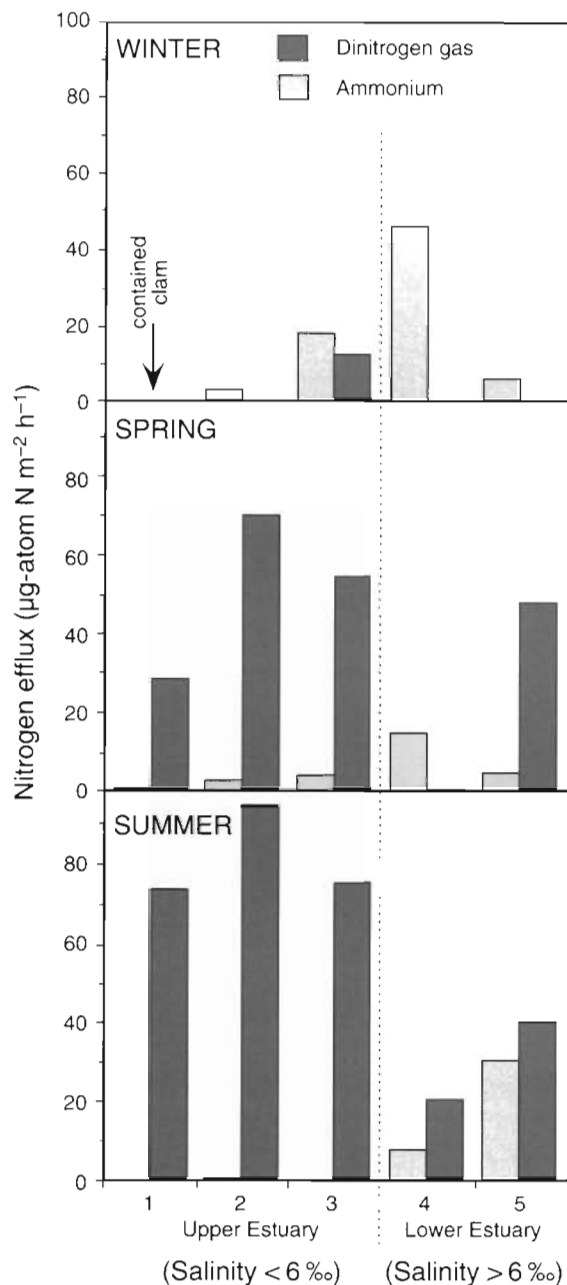


Fig. 3. Seasonal and spatial variation in dinitrogen gas and ammonium efflux from Galveston Bay sediments

relative to saltwater by cation exchange interactions (Gardner et al. 1991, Seitzinger et al. 1991). The effect of NH_4^+ retention in freshwater sediments is that a greater portion of the NH_4^+ would be available for nitrification and, ultimately, denitrification. We did not find a significant correlation between salinity and N_2 or NH_4^+ release. However, the highest measured rates of denitrification occur at salinities less than 6‰. At the same time, fluxes of NH_4^+ are minimal in all of these upper-estuary sediments. This suggests the exis-

Table 7. Analysis of variance (% variance accounted for by pairs of variables, not including Site 1 winter core data) associated with water and sediment characteristics and benthic processes

	Denitrifi- cation	Oxygen consumption	DIC flux
Incubation temperature	52	74	7
Bay water salinity	15 ^a	0	0
Sediment wt % organic C	28	8	0
Sediment wt % total N	10	0	0
Sediment porosity	11	0	3

^a Would be 29 % without Site 2 winter core

tence of a lower salinity limit (of 5 to 6‰) at which cation exchange reactions impair the flux of NH_4^+ from the sediments. Alternatively, factors other than salinity may be of greater importance in creating the observed trend. For example, the higher organic carbon content of the sediment in the upper estuary may provide substrate necessary to support higher rates of microbial activity. The richer sediment may also support a higher density of meio- and macrobenthic organisms which indirectly stimulate denitrification and nitrification through increased sediment ventilation (Pelegri et al. 1994). Sediment weight % organic carbon accounted for 28% of the variability associated with denitrification rates while salinity only accounted for 15% of the variance (Table 7). Other sediment characteristics such as porosity and weight % total nitrogen were more weakly associated with the variance of denitrification, oxygen consumption and DIC flux. Temperature accounted for most of the variation in denitrification (52%) and oxygen consumption (74%) rates indicating a predominance of temporal over spatial factors in determining benthic denitrification rates.

Carbon mineralization

If we make the provisional assumption that no net dissolution or precipitation of carbonaceous sediment has occurred, the flux of DIC from sediments integrates all metabolic activities leading to carbon mineralization. The concurrent measurements of DIC, nutrient and gas fluxes during incubations allows estimation of the C:N ratio of the remineralized organic matter in sediments. A ratio similar to that of 'Redfield' organic material (6.6) is expected if fresh phytoplankton-derived organic matter is remineralized. During the winter, the mean C:N of remineralized material (8.5) was greater than 'Redfield' material, whereas during the spring and summer the ratio was less (4.2 and 2.9, respectively). This decrease could

reflect a shift from utilization of riverine-derived organic material in winter to algal-derived organics in the spring and summer. Alternatively, the observed decrease in the C:N of remineralized organic matter from winter to summer is consistent with the measured increase in the C:N of the remaining sedimentary organic matter (Table 2) and may be due to an increase in the preferential remineralization of nitrogen during this time. Overall, the mean molar C:N benthic efflux (6.2) is much less than the mean C:N in the sediment (12.6), indicating that preferential remineralization of nitrogen does occur.

We believe that most major C and N fluxes were measured in the present study, but other benthic processes could effect the observed rates. The occurrence of carbonate precipitation would cause measured DIC fluxes to be reduced. Although some have found evidence of carbonate precipitation in Texas bays (Morse et al. 1992), more commonly, organic decay produces acidic conditions leading to the possibility of carbonate dissolution (Boudreau 1987, McNichol et al. 1988). Measurements of dissolved calcium in sediment porewaters have shown carbonate precipitation/dissolution to be a small contributor (<1%) to DIC fluxes in Flax Pond, Long Island Sound (New York, USA) (Mackin & Swider 1989) and generally minor in comparison to the contribution by organic carbon decomposition (Aller 1982, Boudreau & Canfield 1988). Another recent study, however, has estimated that carbonate dissolution may at times significantly affect the flux of benthic DIC in a coastal marine setting (Green et al. 1993). Methanogenic and chemoautotrophic bacteria consume CO_2 and would thus reduce the measured DIC flux. Nitrifying bacteria are chemoautotrophs, but given their maximal incorporation rate of 1 mol of bicarbonate for every 5 mol ammonium oxidized (Gundersen & Mountain 1973), inclusion of this factor into our carbon budget would not cause significant changes. At the highest calculated nitrification rate of $87 \mu\text{g-at. N m}^{-2} \text{h}^{-1}$ only $17 \mu\text{g-at. C m}^{-2} \text{h}^{-1}$ would be consumed.

A few other caveats deserve mention. Although significant benthic fluxes of dissolved organic carbon (DOC) have been recorded (Martin & McCorkle 1993), random tests of our systems revealed only small DOC fluxes from Galveston Bay sediment relative to those of DIC. The same result has been reported for other coastal marine systems (Sampou & Oviatt 1991, Canfield & Des Marais 1993). Sediment-water fluxes of dissolved organic nitrogen have been found to be major contributors to the total nitrogen budget in certain environments (Lomstein et al. 1989, Enoksson 1993) but were not measured in the present study. Other benthic processes not considered here include microbial nitrogen fixation and photosynthesis. The

activity of benthic microalgae could certainly impact the cycling of carbon and nitrogen, but *in situ* benthic chamber flux measurements would be needed to adequately evaluate their importance. The possible contribution of NO_3^- reduction to NH_4^+ to the overall degradation of organic matter and the cycling of nitrogen has also been left undetermined.

Benthic carbon and oxygen budgets

An examination of the absolute and relative amounts of carbon mineralized by denitrification and oxygen used by nitrification (Table 6) gives some indication of the relative importance of each of these processes in controlling estuarine sediment-water exchanges. A seasonal trend of note is the increase in relative amount of carbon mineralized by denitrification from the winter to the summer. As for spatial distribution, a greater portion of the carbon mineralization is due to denitrification in upper Galveston Bay (37%) relative to the lower estuary (13%) during all seasons. These trends are likely influenced by the greater availability of sulfate in the lower estuary causing rates of carbon mineralization by sulfate reduction to be greater there.

Nitrate respiration has previously been thought to play a relatively minor role in the overall benthic mineralization of organic material both in estuaries (Fenchel & Blackburn 1979, Sørensen et al. 1979) and coastal marine settings (Jørgensen 1982, Christensen 1989, Jahnke et al. 1989). Jørgensen & Sørensen (1985) found that denitrification and NO_3^- reduction to NH_4^+ in a Danish fjord contributed 3 and 5%, respectively, of the annual organic matter remineralization in the lower estuary and 4 and 33% in the upper estuary. Denitrification however was measured by the acetylene block method which inhibits nitrification. This could result in an underestimation of denitrification and allow more NO_3^- to be available for reduction to NH_4^+ . Our results indicate that some reduction of NO_3^- to NH_4^+ probably occurred, but denitrification alone accounted for roughly one-third of benthic carbon remineralization in Galveston Bay overall, and closer to one-half in the spring and summer upper estuary. Yoon & Benner (1992) found that denitrifiers mineralized carbon at rates at least comparable to those of aerobic heterotrophs in 2 south Texas estuaries. As in Galveston Bay, denitrification was responsible for about 20% of the total carbon mineralized in Washington shelf sediments (Devol & Christensen 1993).

During the winter, almost no nitrification took place in the bay. Because the $\Delta\text{CO}_2/\Delta\text{O}_2$ ratio was nearly always greater than 1 at this time, the occurrence of significant chemical oxygen consumption is unlikely. The majority of SOC during the winter, then, can be

Table 8. A comparison of benthic fluxes from sediments of 4 Gulf of Mexico estuaries

Location	Denitrification rates ($\mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$) ^a				Nitrogen fluxes ($\mu\text{mol m}^{-2} \text{ h}^{-1}$) ^b				Total oxygen consumption ($\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$)		Salinity (‰)		Water residence time (d) ^c	Range of water DIN conc. (mg l^{-1})	Primary production ($\text{g C m}^{-2} \text{ d}^{-1}$)	Sedimentary organic C (%) ^d		Source	
	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Winter	Spring	Summer	Upper				Lower	Upper		Lower
Nueces Estuary, Texas	11	4	40	9	59	43	50	8	10	0	198	261	432	37	36	485	0.05–1.0	0.5–1.0 0.9	Yoon & Benner (1992) R. Scalan (unpubl.)
Guadalupe Estuary, Texas	19	5	24	21	30	14	60	30	10	8	234	465	483	18	26	93	0.1–1	0.7–1.2 0.7	Yoon & Benner (1992) R. Scalan (unpubl.)
Trinity-San Jacinto Estuary, Texas (Galveston Bay)	2	0	25	12	40	15	8	18	–6	2	64	171	269	2	13	70	0.05–0.5	2.2 0.6	This study Morse et al. (1993)
Ochlockonee Bay, Florida	25	0	64	91	36	38	16	21	12	14	667	731	546	3	13	4.5	0.01–0.04	0.7 (3.0–7.0)	Seitzinger (1987)

^a Measured as N₂ production in all cases. Value is mean of upper- (i.e. lower salinity regime) and lower-estuary sites. Summer fluxes for Guadalupe Estuary were measured in March, April and June

^b Annually averaged nitrogen fluxes were measured in May only for Nueces Estuary and May and October for Guadalupe Estuary. Positive values are from the sediment to the water

^c Productivity, DIN and residence data for Texas estuaries are calculated using data in TWDB & TPWD (1992)

^d Organic carbon content of Ochlockonee Bay sediment is an estimate based on reported measurements of Apalachee and Apalachicola Bay (bays to the east and west) sediments (NOAA 1991)

^a Measured as N_2 production in all cases. Value is mean of upper- (i.e. lower salinity regime) and lower-estuary sites. Summer fluxes for Guadalupe Estuary were measured in March, April and June

^b Annually averaged nitrogen fluxes were measured in May only for Nueces Estuary and May and October for Guadalupe Estuary. Positive values are from the sediment to the water

^c Productivity, DIN and residence data for Texas estuaries are calculated using data in TWDB & TPWD (1992)

^d Organic carbon content of Ochlockonee Bay sediment is an estimate based on reported measurements of Apalachee and Apalachicola Bay (bays to the east and west) sediments (NOAA 1991)

attributed to aerobic respiration. Increases in nitrification during the spring and summer result in increases in both the absolute and the relative amount of oxygen consumption by nitrification. Annually, nitrification consumed 30% of the SOC with twice as much occurring in the upper estuary relative to the lower estuary. The nitrification rates calculated for Galveston Bay sediments are in the range of those previously recorded for Narragansett Bay, Rhode Island, USA (Seitzinger et al. 1984), Ochlockonee Bay, Florida, USA (Seitzinger 1987) and Nueces and Guadalupe Estuaries, Texas (Yoon & Benner 1992). Relative oxygen consumption by nitrification in these estuaries (20 to 30%) also matches that of Galveston Bay.

Interestuary comparisons

Denitrification rates measured in various estuarine and coastal marine sediments range widely from 0 to $900 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ (Seitzinger 1988). In order to make direct comparisons and to approach a better understanding of the factors controlling denitrification rates, we have compiled information on 4 Gulf of Mexico estuaries (Table 8). Denitrification rates were measured by N_2 evolution in these studies and are therefore directly comparable. Additionally, seasonal temperature variation is similar among these 4 estuaries. Overall, the denitrification and sedimentary oxygen consumption rates observed in Galveston Bay sediments are on the low end of the range of those previously published. This is surprising given that Galveston Bay has the highest primary productivity among the 4 estuaries (TWDB & TPWD 1992). Ochlockonee Bay and Galveston Bay are the least saline and have the shortest water and DIN residence times but display the highest and lowest benthic denitrification rates, respectively, of the 4 estuaries examined. Only mean sedimentary organic carbon content was found to be positively correlated with denitrification rates across these estuaries ($r = 0.86$, $p < 0.01$). Though the organic carbon data were gathered from a variety of sources and probably vary considerably from core to core, this factor, after temperature, does appear to best explain both intra- and interestuary variation in denitrification rates. The effect, however, may be an indirect one as higher organic carbon content supports greater benthos abundances. Some studies have found decreases in benthic metazoan abundance from Nueces to Guadalupe to Trinity estuary (Montagna & Kalke 1992, TWDB & TPWD 1992) mirroring the trend in denitrification rates. Benthos abundance, however, is sensitive to changes in salinity, oxygen concentration and other parameters, which can fluctuate seasonally and annually.

Table 9. Efficiency of nitrogen removal from Gulf of Mexico estuaries by denitrification

Location	Mass loading of N nutrients ^a ($\text{g m}^{-2} \text{yr}^{-1}$)		N removed by denitrification ($\text{g m}^{-2} \text{yr}^{-1}$)	Percent of total N removed by denitrification	Source
	River load	Total load			
Nueces Estuary	1.5	4.7	6.4	136	Yoon & Benner (1992)
Guadalupe Estuary	16.9	21.7	4.9	23	Yoon & Benner (1992)
Trinity-San Jacinto Estuary	17.0	32.9	4.5	14	This study
Ochlockonee Bay	16.6	17.3	9.0	52	Seitzinger (1987)

^a From TWBD & TPWD (1992). Based on 1977 to 1987 data

Among the 4 estuaries, a direct correlation was found between bay water salinity and NH_4^+ benthic efflux ($r = 0.723$, $p < 0.05$) as suggested by the cation exchange hypothesis of Gardner et al. (1991). However, the higher NH_4^+ residence time in sediments overlain by less saline waters does not seem to translate directly into higher rates of nitrification and denitrification. Higher benthic fluxes of nitrate and nitrite from the sediments of these 3 other estuaries may cause denitrification to be less tightly coupled to nitrification than in Galveston Bay and therefore independent of salinity variation.

Maximum denitrification rates in Galveston, Nueces and Guadalupe estuaries occur in the summer and appear to vary mainly with temperature. In contrast, sedimentary denitrification maxima have been found to occur in the spring in Ochlockonee Bay (Seitzinger 1987), Norsminde Fjord, Denmark (Jørgensen & Sørensen 1985, Binnerup et al. 1992) and Aarhus Bight, Denmark (Jensen et al. 1988). It may be that denitrification is primarily controlled by substrate availability in these estuaries and thus is strongly affected by the increased delivery of organic substrate to the sediment resulting from spring blooms (Jensen et al. 1988) or river discharge. Nutrient delivery to Texas estuaries does not vary to the extent of other estuaries which experience seasonal stratification or spring-melt runoff episodes. Thus, spring blooms are not as dramatic and sedimentary organic carbon content does not vary greatly through the year. This combination of factors causes denitrification rates in Galveston Bay to vary seasonally with temperature and spatially with substrate availability.

As with most estuaries, denitrification is an important sink for the nitrogen entering Galveston Bay. Using $37 \mu\text{g-at. N m}^{-2} \text{h}^{-1}$ as the annual mean rate of denitrification, it is calculated that 14% of the dissolved inorganic nitrogen entering Galveston Bay from all sources is removed by denitrification (Table 9). Denitrification removes an amount of nitrogen equivalent to 26% of the riverine nitrogen inputs to Galveston Bay. This removal efficiency is low compared to

that calculated for other estuaries, commonly between 40 and 50% (Seitzinger 1988). However, the anthropogenic nitrogen inputs to Galveston Bay are an unusually large portion of the nitrogen entering the estuary. Some estuaries seem to maintain a denitrification removal efficiency in the range of 40 to 50% even when heavily loaded with anthropogenic nitrogen inputs, e.g. Tejo Estuary, Portugal (Seitzinger 1987), Tama Estuary, Japan (Nishio et al. 1982), Delaware Bay (Seitzinger 1988), and Nueces Estuary (Yoon & Benner 1992). The relatively lower nitrogen removal efficiency by Galveston Bay denitrifiers may be due, ultimately, to a paucity of utilizable organic substrate and its relatively less dense benthic invertebrate population.

The potential importance of infaunal bioturbation should be noted. Through the addition of nitrogenous waste products, enhancement of nitrification through the oxygenation of deeper sediment layers and the creation of anoxic microenvironments, the burrowing activity of metazoans may greatly increase the activity of denitrifiers and microbes in general. The presence of 1 clam in chamber 1 of the winter incubation apparently increased the production of nitrogen gas to 10 times the mean rate in the other chambers during the same period and promoted the exposure of reduced species within the sediment to chemical oxidation. The enhancement effect of macro- and meiofaunal irrigation has been noted in many other studies as well (e.g. Aller 1982, Binnerup et al. 1992, Devol & Christensen 1993, Pelegri et al. 1994). This being so, one would expect the amount of denitrification and removal efficiency of nitrogen in estuaries to vary, perhaps greatly, from year to year with such factors as freshwater inflow, water quality and substrate quality, which all strongly affect the health of benthic metazoan communities. Interestuary comparisons carried out during the same year and season measuring all of these parameters in addition to denitrification would greatly improve our understanding of the factors controlling the estuarine nitrogen cycle.

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This article was presented by S. Y. Newell (Senior Editorial Advisor), Sapelo Island, Georgia, USA

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