Denitrification in Galveston Bay
1997 Annual Report

A report submitted to the
Texas Water Development Board

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I. Introduction

The cycling of nitrogen (N) between the compartments of a given ecosystem is driven primarily by microbially-mediated processes, including N uptake, dinitrogen (N_2) fixation, ammonification, N assimilation, nitrification, dissimilatory nitrate reduction to ammonium, and denitrification (Blackburn and Sørensen 1988; Cole and Ferguson 1988). Physical dynamics, such as advection, sedimentation, and sediment resuspension, also contribute to the movement of N between compartments; however, microbially mediated processes ultimately transform N between forms and thus regulate the magnitude of potential N loss via denitrification. Dinitrogen can serve as a nutritional N source to only a limited suite of microorganisms (N_2 fixers; Knowles 1982; Howarth et al. 1988; Zumft et al. 1988). Thus, the process of denitrification serves to remove combined N from the biologically available pool as denitrifying microorganisms transform nitrate or nitrite to gaseous forms, N_2 or nitrous oxide (N_2O). Denitrifying bacteria respire nitrate primarily under conditions low oxygen (O_2) concentrations (< 10 μM; Knowles 1982; Tiedje et al. 1989); however, some O_2 tolerant denitrifiers are known (Robertson and Kuenen 1991).

Since denitrification is a sink for N, it is important to identify the environmental and physiological factors that regulate the process. Denitrification is frequently controlled by the nitrate concentration but temperature and the concentration of organic carbon, O_2 and hydrogen sulfide (HS^-) also influence activity (Koike and Sørensen 1988; Joye and Paerl 1993). Sources of nitrate utilized by denitrifiers include nitrification, advection of nitrate-rich ground water, and/or diffusion or advection (bioturbation enhanced) of nitrate from the overlying water column (Vanderborght and Billen 1975; Grundmanis and Murray 1977; Henriksen and Kemp 1988). Nitrification and bioturbation (advective exchange) are often positively correlated because bioturbation can stimulate nitrification by increasing O_2 availability

(Kristensen 1988). Together, these two processes may regulate pore water nitrate concentration and thus influence denitrification rates (Jenkins and Kemp 1984; Andersen et al. 1984; Caffrey 1995).

A large fraction of N cycling in coastal ecosystems occurs in sediment environments. This is particularly true in shallow ecosystems like Galveston Bay. In terms of its sedimentary cycle, N, as either particulate organic or inorganic forms, is delivered to the sediment, where recycling (regeneration) occurs (Joye et al. 1998). After internal regeneration processes, some fraction of regenerated N is returned to the water column as dissolved inorganic N [DIN = nitrite + nitrate + ammonium]: this can be considered the "regenerated" fraction. Another portion may be cycled through nitrification and then denitrification which leads to the loss of N gases (N_2 or N_2O); this can be considered the "denitrified" or lost fraction. Finally, some portion of regenerated N may be permanently buried in the sediment. The buried fraction represents a long term sink for N in the system. However, in the context of nutrient regeneration and the sustenance of ecosystem production on the short term, the difference between the regenerated and denitrified fractions is the most important consideration (Joye et al. 1998).

In many coastal systems, combined N loss occurs largely via coupled denitrification. The coupled denitrification rate is a function of 1) the nitrification rate, and, 2) the extent of coupling between nitrification and denitrification (Jenkins and Kemp 1984; Seitzinger 1988). Denitrification rates in coastal sediments range between 1 - 6 mmol N m^{-2} d^{-1} (Seitzinger 1988), while nitrification rates range between 0 - 5 mmol N m^{-2} d^{-1} (Henriksen and Kemp 1988). Spatio-temporal variations in temperature, organic carbon supply, and O_2 and HS^- concentration may affect nitrification and, thus indirectly influence denitrification (Henriksen and Kemp

1988; Joye and Hollibaugh 1995) or coupling between nitrification and denitrification (Nishio et al. 1983; Jenkins and Kemp 1984; Christensen et al. 1987; Caffrey and Kemp 1990; Kemp et al. 1990; Binnerup and Sørensen 1992).

The Galveston Bay estuary, the second largest estuarine system along the Texas coast, is surrounded by an urbanized metropolis. Approximately 3.5 million people inhabit the Galveston Bay watershed, and, of those, roughly 20% live within 2 miles of the Bay or its tidal tributaries. The edges of Galveston Bay also serve as home to 30% of the United State's oil refining capacity and to the Port of Houston, the nation's 3rd largest port. The impacts of industrial and population pressures on the Galveston Bay ecosystem are numerous and the system has been altered significantly from its pristine state.

The health of coastal ecosystems depends greatly on watershed management. A recent Texas Water Development Board (TWDB) Water Plan projects that the state population will double over the next 25 years. More than half of this estimated increase (36 million people) is expected to live along the coast. With respect to Galveston Bay, the result of the increased freshwater demand may be a shifting of freshwater and nutrients from riverine and agricultural runoff to more inputs from urban-area wastewater discharges. This could mean shifts in total nutrient loading rates as well as more uniform delivery of nutrients, as the pulsed nature of freshwater runoff and diffuse inputs is replaced by a more steady input of point sources of nutrients (e.g., industrial and municipal sewage derived inputs).

Planning for the future of the Galveston Bay ecosystem requires integrating the municipal and industrial water needs of the surrounding watershed with the needs of the estuary. Decreases in freshwater inflow reduce the loading of particulate and

dissolved nutrient inputs, modifications of salinity structure, and alterations of residence time. Feedback and interaction between these three parameters (nutrient inputs, salinity structure and residence time) can, in turn, serve to regulate or influence internal nutrient cycling. Properly modeling the ecological and geochemical responses of the Galveston Bay system to changing freshwater inputs requires accurate measurements of processes made over long (preferably seasonal) time scales.

In the process of determining estuary inflow requirements, nutrient loading from freshwater may be as important a consideration as inflows needed to maintain salinity gradients or other factors. Assessment of the nutrient inputs necessary to support production requires adequate knowledge of the nutrient budgets of the estuarine system, and work has been done to compile meaningful budgets for Galveston Bay (Brock 1994; Brock et al. 1996). However, those budget exercises revealed areas where rates of important processes were not well known, e.g., denitrification rates. Furthermore, without good knowledge of how nutrient processes vary with inflow and other parameters, the budgets were relatively static and not well suited for predicting system behavior under different inflow regimes. Denitrification is a key term in the system N budget because the availability of N often limits production in coastal ecosystems and denitrification can regulate N levels in shallow coastal systems. Thus, a detailed understanding of the spatio-temporal trends in denitrification activity must be included in any system level N budget in order to properly predict responses to changing hydrologic and environmental parameters.

Previous estimates of denitrification in Galveston Bay sediments have provided two strikingly different scenarios. Measurements at five sites on three separate occasions during a year yields an average denitrification rate of 43 μmol N m^{-2} hr^{-1} or 1 mmol N m^{-2} d^{-1} (Zimmerman and Benner (1994). Modeling of these data

suggests that denitrification removes 7-14% of the N on a bay-wide basis (Brock et al. 1996). In contrast, Rowe et al. (submitted) estimate a bay-wide average denitrification rate of 10 mmol N m^{-2} d^{-1} from benthic flux O:N stoichiometry. This estimate of denitrification suggest that >50% of N mineralized in sediments is lost as N_2 gas and, more importantly, that 66% of the N input to the Galveston Bay system is removed via denitrification (Rowe et al. submitted). Obviously, the differences between these two studies raises serious questions regarding the importance of denitrification in the N budget of Galveston Bay. However, neither the Zimmerman and Benner nor the Rowe et al. studies measured denitrification rates directly and *in situ*. Further, only the Zimmerman and Benner study measured rates at the same stations during different seasons. By directly measuring denitrification rates at a series of stations over several annual cycles, it is hoped that better estimates of denitrification and an improved N budget for Galveston Bay can be developed.

Our study began in 1996 and will continue through the end of 1998. The objectives of the current study were to continue our examination of denitrification in Galveston Bay, to assess denitrification in the context of the net sediment N budget and in terms of net carbon and oxygen budgets, and to elucidate the environmental factors influencing denitrification over longer time periods.

II. Methods

Study sites. During the 1997 sampling year, we continued working at 4 stations along the Trinity River salinity gradient and at the Texas City station (Joye and An 1997; Fig. 1A and B). Data were collected in January, April, July, August, and November.

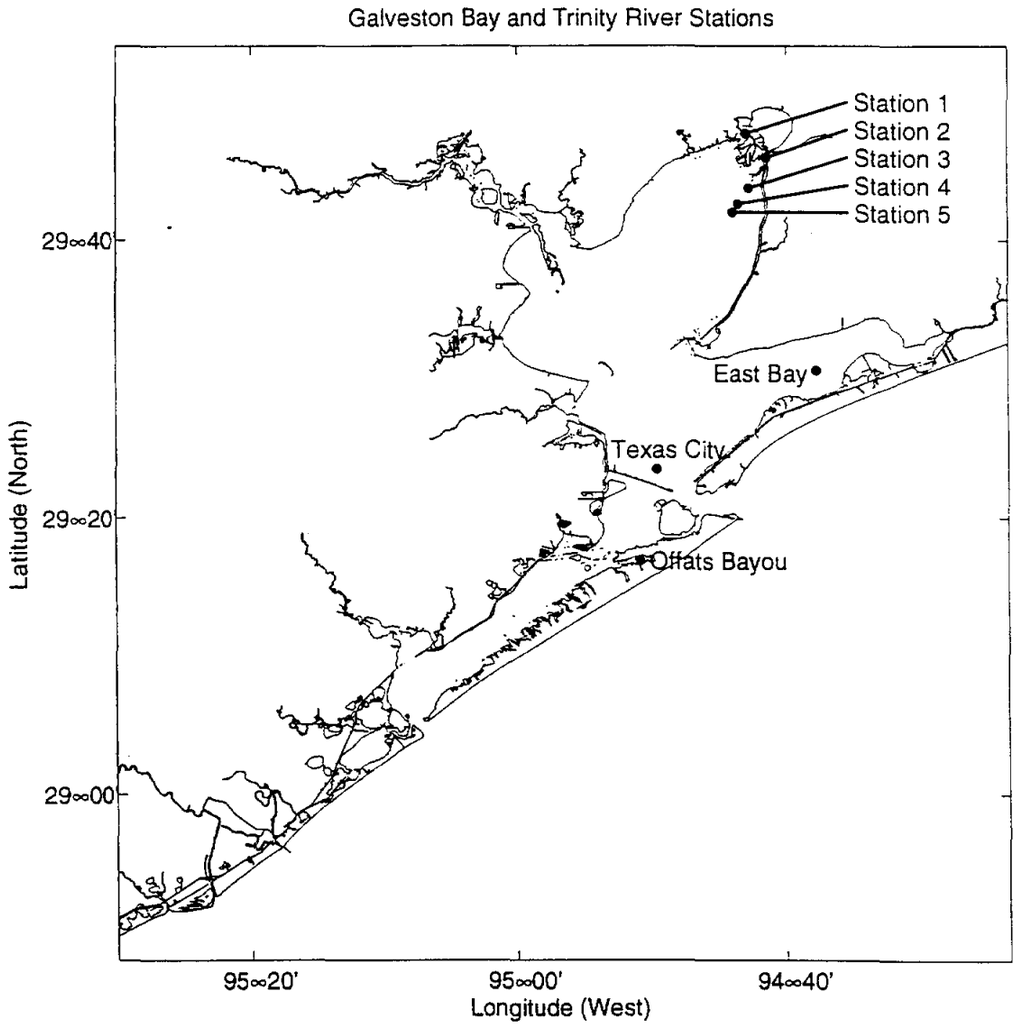

Figure 1a. Locations of Galveston Bay, Texas, sampling stations.

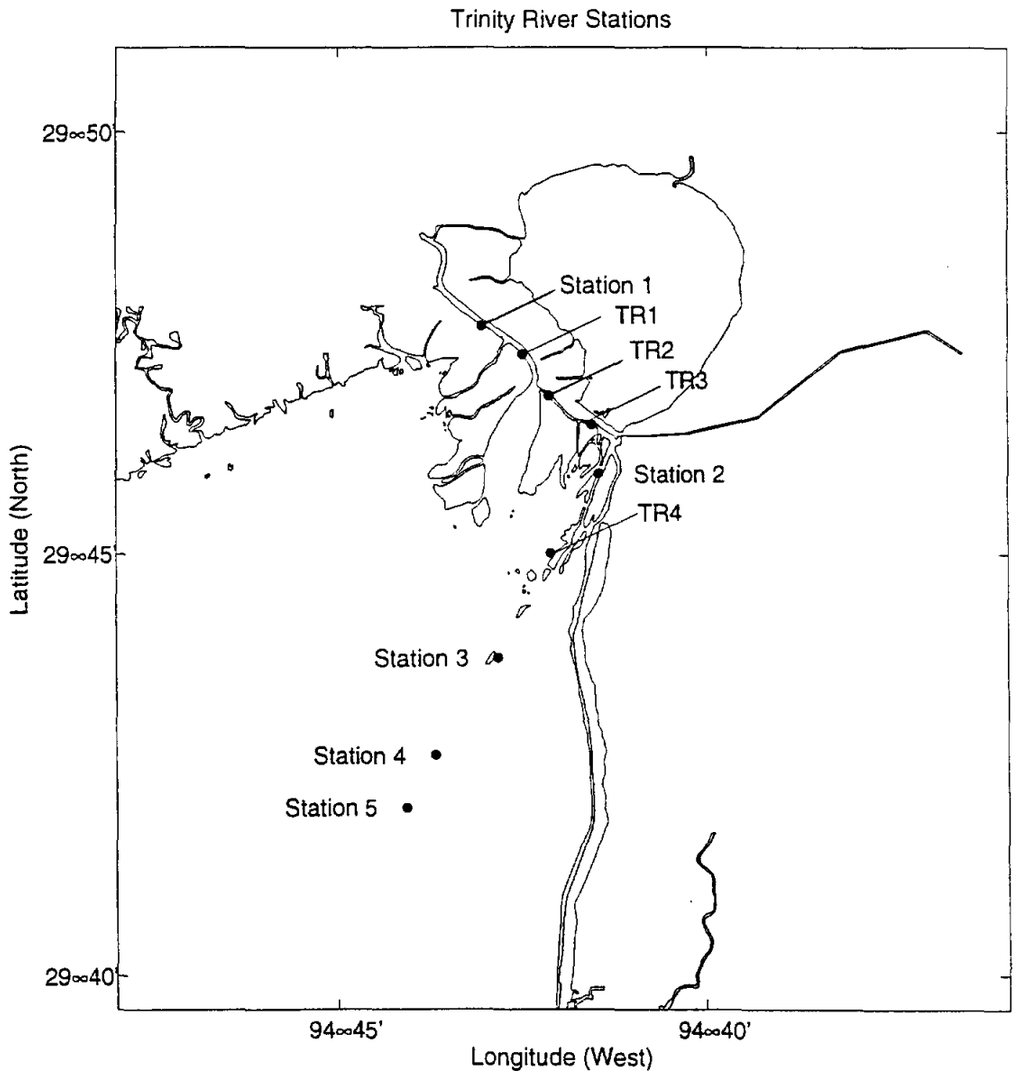

Figure 1b. Detailed view of Trinity River Delta sampling stations (process stations are denoted Station # while transect stations are denoted TR #).

We added two additional stations, one in the East Bay and one in the Trinity Delta region (Station 5). These stations were sampled during August of 1997 and will be sampled again during April and October of 1998. Salinity at the Trinity stations varied between 0 and 8 parts per thousand during the 1997 sampling season as compared to a range of 0 to 15 parts per thousand during the 1996 sampling season. Four transect stations were also monitored along the Trinity salinity gradient. These stations were interspersed at approximately 0.5 km intervals between the primary sampling stations. Only surface and bottom nutrient and dissolved gas concentrations were determined at the transect stations (Fig. 1B).

Water column and sediment variables. A suite of environmental variables were measured at each of the stations. A Hydrolab DataSonde® Multiprobe was used to collect water column profiles of temperature, salinity and dissolved oxygen (O_2) concentration. Samples for the determination of nutrient (NH_4^+, NO_2^-+NO_3^-, and HPO_4^{2-}) and dissolved gas (O_2, N_2, and dissolved inorganic carbon, DIC) concentrations were collected from ca. 0.25 m below the surface and from ca. 0.25 m above the bottom using a Niskin bottle. Approximately 40 mL of water was filtered through a Whatman GF/F (0.7 μm optimal pore size) filter into a plastic bottle. Samples were immediately frozen and stored for subsequent nutrient analysis. Triplicate dissolved O_2 and N_2 gas samples were collected, without introducing bubbles, into gas-tight glass syringes (Glass Pak®) and stored at 4 °C until analysis via gas chromatography approximately 4 days later (An and Joye 1997). The syringes

were filled with He-purged water before sampling to reduce the possibility for atmospheric contamination. Syringes were rinsed by drawing ca. 3 mL of sample into the syringe, then dispelling that volume and collecting a "clean" 10 mL volume. Dissolved inorganic carbon samples were collected into 10 mL vials by slowly overfilling (2X volume) without introducing bubbles. Samples were fixed with mercuric chloride (0.5%) upon collection, capped with teflon coated screw caps without introducing a headspace, and stored at 4° C for future analysis.

Nitrate + nitrite (denoted NO_3^- on figs. and tables) and phosphate concentrations were determined using standard methods on an Alpkem FlowSolution 3000 Autoanalyzer (Joye et al. 1997). Ammonium concentrations were determined spectrophotometrically using the phenol hypochlorite method (Joye et al. 1998). Dissolved inorganic carbon was quantified via coulometric titration (Joye and An 1997) while dissolved O_2, N_2, and Ar concentrations were quantified using gas chromatography (An and Joye 1997).

Sediment cores (50 cm long and 5 cm wide) were collected by scuba divers so that sediment pore water nutrient profiles, chlorophyll *a* concentration, porosity, and grain size distribution could be quantified. Pore waters were collected using a Reeburg Sediment Squeezer (Joye and An 1997). Briefly, pore water was expressed from sediment under a pressurized N_2 atmosphere. Next, the pore water was passed through a GF/F filter into an acid-cleaned, deionized water rinsed 7 mL glass

scintillation vial. Samples were immediately frozen and stored as such until nutrient concentrations were determined (as outlined above). The pore water free sediment (mud cake) was frozen for the future determination of % organic matter, % organic nitrogen and carbon, and photopigment concentration; % organic and CHN analyses are currently being completed. Percent organic (loss on ignition) will be estimated from the weight loss after combusting at 650 °C for six hours. Percent organic carbon and nitrogen are determined using a Carlo Erba NA1500 elemental analyzer. For chlorophyll *a* determination, a 2-3 gram sub-sample of the mud-cake was placed into a 20 mL centrifuge vial containing 15 mL of HPLC grade acetone (90%) and milliQ water (10%). After 24 hours of extraction in the dark in a refrigerator, the tubes were centrifuged at 4000 rpm for 2 min. The supernatant was collected and the chlorophyll *a* fluorescence was measured using a Turner fluorometer (Fenchel and Straarup 1971). Concentrations were converted to μg chlorophyll *a* (cc wet sediment)$^{-1}$. Areal distributions (mg chlorophyll *a* m^{-2}) were obtained by integrating the concentration profile over depth.

Duplicate samples for porosity determination were collected at 2-5 cm intervals throughout the length of the core. Porosity was estimated from the weight loss after drying at 60° for 48 hours. Grain size distribution was estimated by determining the amount (mass) of sediment passing through a 63 μm sieve. Sediment greater than 63 μm is considered coarse grained (sand) while material passing through the sieve is considered fine grained (silt, clay).

The gradient in pore water concentration was determined using a non-linear fitting routine (Kaleidograph®). Then the sediment-water interface gradient was plugged into a Fickian diffusion equation to estimate the sediment-water flux of each nutrient. Comparison between calculated and observed fluxes were made when the curve fits to obtain the gradient at the sediment-water interface yielded r^2 values exceeding 0.9 (Joye and An 1997). When r^2 values were < 0.9, the relationship was not considered significant.

Potential denitrification. Potential denitrification rates were examined using sediment slurry incubations (Joye and An 1997; An and Joye 1997). Surface sediment (0-5 cm) was collected from Station 4 in the Trinity River Delta in November of 1997. The sediment was passed through a 1 mm mesh sieve to remove macrofauna and was then homogenized. Approximately 10 mL of sieved sediment was placed into a 75 mL serum bottle. Thirty mL of station water was then added to the bottle and the slurry was gently mixed. The slurries were amended with either nitrate (0 - 1000 μM), nitrate + glucose (0 - 1000 μM) or nitrate + sulfide (0 - 1000 μM) to determine the relative importance of N versus C substrates on denitrification rates and to assess whether or not denitrification rates were sensitive to the presence of hydrogen sulfide.

A headspace samples were collected initially (time zero) after shaking the bottles to achieve equilibrium between aqueous and dissolved gas phases. Nitrate

amended bottles were incubated for 48 hours at either high (23 °C) or low temperature (4 °C). Nitrate + glucose and nitrate + sulfide amended bottles were incubated at field (23 °C) temperatures only. Following incubation, bottles were vigorously shaken to assure equilibration with the headspace and a gas-phase sample was collected into a gas tight syringe to minimize atmospheric contamination. Gas concentrations were determined using gas chromatography, as described above.

III. Results and Discussion

Water column temperature, salinity and dissolved oxygen distribution.

Physico-chemical characteristics for the study sites throughout the 1996 and 1997 sampling periods are presented in Table 1. The Trinity River stations varied from 1.5 to 3 m in depth. Despite the shallow depths, temperature stratification was frequent, with surface temperatures exceeding bottom temperatures by 0.3 to 2 °C. Temperatures at the Texas City site were similar to those measured at the Trinity stations. Salinity at most of the Trinity stations was zero during 1997, except during August. Salinity at the Texas City station was lowest during April 1997 (1 ppt) and was highest (~ 30 ppt) during summer. Dissolved O_2 concentrations were highest during winter when salinity was lowest (Table 1). Significant surface-bottom differences in dissolved O_2 concentration were apparent at all stations during most sampling periods (see below). Our physico-chemical data was similar to that collected in other parts of Galveston Bay by the TNRCC monitoring program with respect to temperature, salinity and dissolved O_2 distribution (Fig. 2). These

Table 1. Locations and environmental factors at the Trinity River sampling and transect stations
See Figure 1b for the location of the transect stations.

		Station													
		1		2		3		4		5		TC		EB	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Location															
	Longitude	94.43.063		94.41.511		94.42.828		94.43.667		94.44.063		94.49.659		94.37.823	
	Latitude	29.47.700		29.46.348		29.43.771		29.42.613		29.41.995		29.23.516		29.30.650	
Depth (m)		2.1		3		1.5		1.5		2		4.5		2.1	
Temperature (°C)															
	1996 June	28	28	-	-	28.5	27	28.5	28.2	-	-	-	-	-	-
	July	31.3	30.6	32	30	30.5	27.5	31	-	-	-	-	-	-	-
	Aug.	28.3	28	29	28	28.2	26.9	28.5	28	-	-	-		-	-
	Oct.	-	-	-	-	-	-	18.5	17	-	-	21.5	20.1	-	-
	1997 Jan	14.3	14.3			14	14.1	13.8	13.8	-	-	14.8	15.2	-	-
	Apr	18.7	18.7	19.3	19.3	20.1	19.9	18.9	18.7	-	-	20	19.7	-	-
	July	30.6	30.6	32	29.7	32.8	32.8	29.6	29.6	-	-	31.4	31.2	-	-
	Aug.	31.6	30.7	27.8	27.9	27.9	26.9	31.6	31.6	31.2	31.2	31.1	31	31.6	30.8
	Nov.	15.6	15.6	15.4	15.4	15.3	15.3	129	12.9	-	-	-	-	-	-
	1998 Jan.	14.5	-	14.2	-	14.3	14.4	14.1	14.2	-	-	14.5	15.2	-	-
Salinity (ppt)															
	1996 June	-	0	-	-	-	-	-	-	-	-	-	-		
	July	0	0	1.5	-	10	12	15	-	-	-	16	17	-	-
	Aug.	0	0	0	0	0	0	-	-	-	-	-	-	-	-
	Oct.	0	0	0	0	0	0	-	-	-	-	-	-	-	-
	1997 Jan	0	0	0	0	0	0	1.5	1.5	-	-	6.3	7.2	-	-
	Apr	0	0	0	0	0	0	0	0	-	-	0.9	1.2	-	-
	July	0	0	0	0	0	0	0.4	0.4	-	-	20.9	23.8	-	-
	Aug.	0	0	3.3	3.4	4.1	4.1	5.2	5.3	7.6	7.8	29.6	29.8	12.2	12.5
	Nov.	0	0	0	0	0.4	0.4	0.4	0.4	-	-	-	-	-	-
	1998 Jan.	0	0	0	0	0	0	0	0	-	-	6	13	-	-
Oxygen (ml L^{-1})															
	1996 June	9.8	6.5	-	-	9.1	6.6	7.7	6.1	-	-	-	-	-	-
	July	7.2	6.4	8.1	5.0	5.6	4.2	-	6.6	-	-	-	-	-	-
	Aug.	6.8	5.2	-	5.4	10.8	7.5	8.6	5.8	-	-		-	-	-
	Oct.	-	-	-	-	-	-	8.7	7.9	-	-	8.4	6.2	-	-
	1997 Jan	10.2	10	-	-	10	10	10.2	10.2	-	-	9.2	8.5	-	-
	Apr	7.7	7.6	7.6	7.5	8.3	7.9	8.3	8.2	-	-	8.3	7.8	-	-
	July	6.8	5.6	6.7	4.3	6.3	6.2	6.9	6.6	-	-	7.1	5.7	-	-
	Aug.	7.3	4.6	6.7	6.4	7.5	7	6.5	6.3	6.4	5.7	5.5	5	8.9	6.5
	Nov.	9.8	9.3	9	9.1	9.1	9.1	9.8	9.6	-	-	-	-	-	-
	1998 Jan.	10	9.9	9.5	9.3	10.2	10.2	10.5	10.5	-	-	9.5	8.7	-	-

Table 1. Continued

		Transect Station									
		OB		1		2		3		4	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Location											
	Longitude	94.50.87		94.42.551		94.42.275		94.41.479		94.41.991	
	Latitude	29.16.91		29.47.41		29.46.907		29.45.947		29.44.864	
Depth (m)		5.1		3.6		3.6		3.6		3	
Temperature (°C)											
	1996 June	-	-	-	-	28	28	-	-	-	-
	July	-	-	31	31.5	30.5	30.5	31.5	32	31.1	28.2
	Aug.	28	27.2	-	-	-	-	-	-	-	27
	Oct.	23	22.5	-	-	-	-	-	-	-	-
	1997 Jan	-	-	14.3	14.3	14.2	14.3	14.2	14.2	14	14.2
	Apr	-	-	-	-	-	-	-	-	-	-
	July	-	-	31.5	29	31.5	29.6	-	-	31.3	29.9
	Aug.	-	-	31.3	31.1	31.2	31	30.7	30	29.7	28.9
	Nov.	-	-	15.5	15.5	15.5	15.5	15.5	15.5		
	1998 Jan.	-	-	14.3	14.3	14.2	14.3	14.1	14.3	14.2	14.2
Salinity (ppt)											
	1996 June	-	-	-		3		-		-	
	July	32	34	-	-	0	-	-	-	0	10
	Aug.	-	-	-	-	-	-	-	-	-	-
	Oct.	-	-	-	-	-	-	-	-	-	-
	1997 Jan	-	-	0	0	0	0	0	0	0	0
	Apr	-	-	-	-	-	-	-	-	-	-
	July	-	-	0	0	0	0	-	-	0	0
	Aug.	-	-	0	0	0	0	0.4	2.7	1.1	2.3
	Nov.	-	-	0	0	0	0	0	0	-	-
	1998 Jan.	-	-	0	0	0	0	0	0	0	0
Oxygen (ml L^{-1})											
	1996 June	-	-	6.4	-	7.2	5.6	-	6.5	-	-
	July	-	-	7.2	6.2	6.6	4.3	6.4	4.1	5.8	3.9
	Aug.	10.2	4.3	-	-	-	-	-	-	9.3	7.6
	Oct.	8.2	4.2	-	-	-	-	-	-	-	-
	1997 Jan	-	-	10.3	9.8	10.3	9.5	10.1	9.8	10.3	9.7
	Apr	-	-	-	-	-	-	-	-	-	-
	July	-	-	7.3	4.7	7.3	4.6	-	-	8.2	5.4
	Aug.	-	-	7.2	5.9	6.5	6	7.7	5.4	7.7	5.6
	Nov.	-	-	10	9.5	9.2	9	9.2	9	-	-
	1998 Jan.	-	-	9.8	9.7	10.1	10.1	9.7	9.7	9.6	9.5

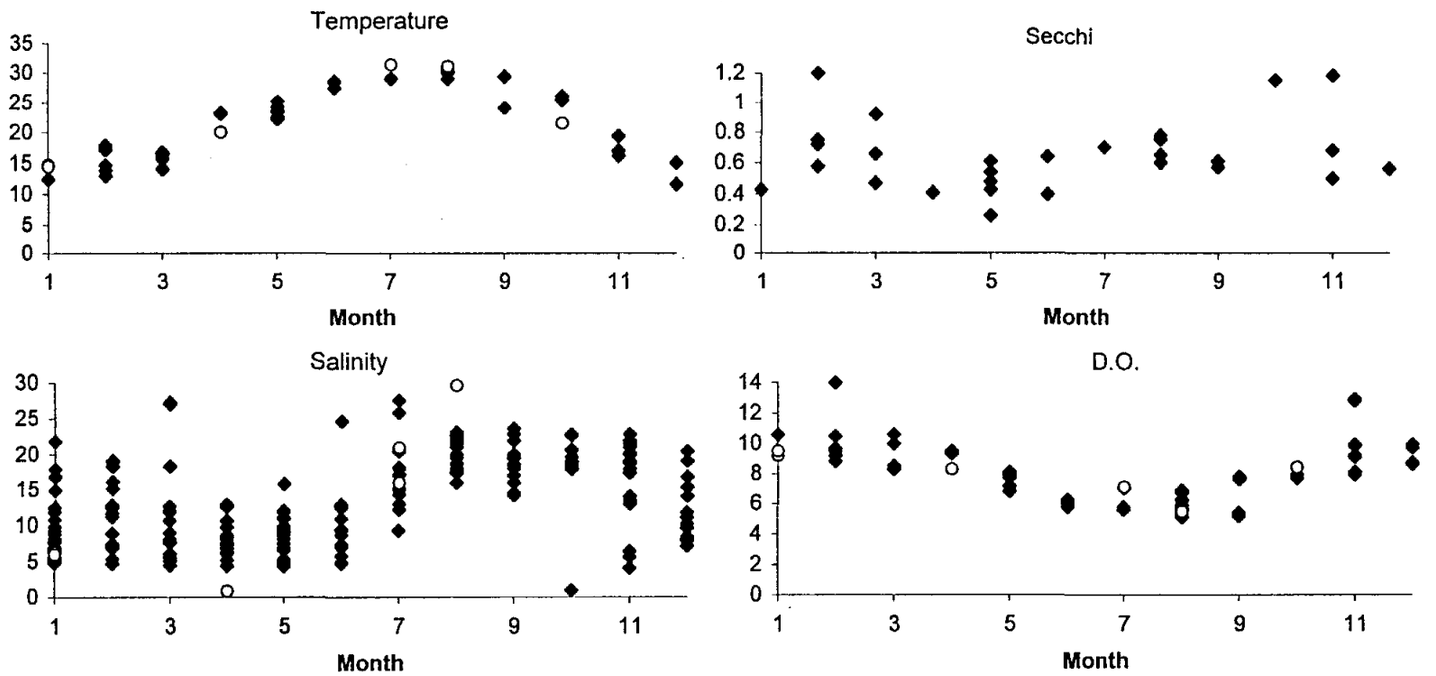

Figure 2. Seasonal variation of physio-chemical parameters at TNRCC Station 13366. Black symbols represent TNRCC data collected between 1990-1997 while open symbols reflect data collected during this study at our Texas City station. The units are: Temperature - ° C; Secchi depth - meters; Salinity - ppt; and dissovled oxygen (D. O.) - mg/L.

data were collected from the TNRCC Station 13366, which is near our Texas City Station. Secchi depth throughout the bay averages 0.6 - 0.7 m with a range of 0.2 to 1.2 m (Fig. 2).

The seasonal variability in the depth distribution of temperature and dissolved O_2 concentration at our stations are shown in Figs. 3 and 4. The water column temperature gradients were large when considering the depth over which they occurred (0.3 to 1 °C over 1.2 - 4.5 m so $\Delta T/\Delta z = 0.07 - 0.8$; Fig. 3). The dissolved O_2 (D.O.) gradient was even more obvious and significant (Fig. 4). Thus, even if the water column was only slightly thermally stratified, strong chemical stratification with respect to D.O. concentration developed. The most striking gradients in D.O. concentration were observed in the shallow (< 2m) Trinity River stations during summer . During April, the D.O. gradient was reduced. Similar to the Trinity stations, the East Bay site exhibited a notable gradient in water column D.O. over a 2 m deep water column. The difference in surface and bottom D.O. concentration was obtained by subtracting the bottom water O_2 concentration from the surface water O_2 concentration (Fig. 5). The largest differences, up to 4 mg O_2 L^{-1}, were consistently observed in the Trinity stations during summer.

The presence of stratification with respect to D.O. concentration is related to the mixing regime, and this is probably related to freshwater inflow. During periods of low flow and reduced turbulent mixing, biological O_2 consumption creates chemical

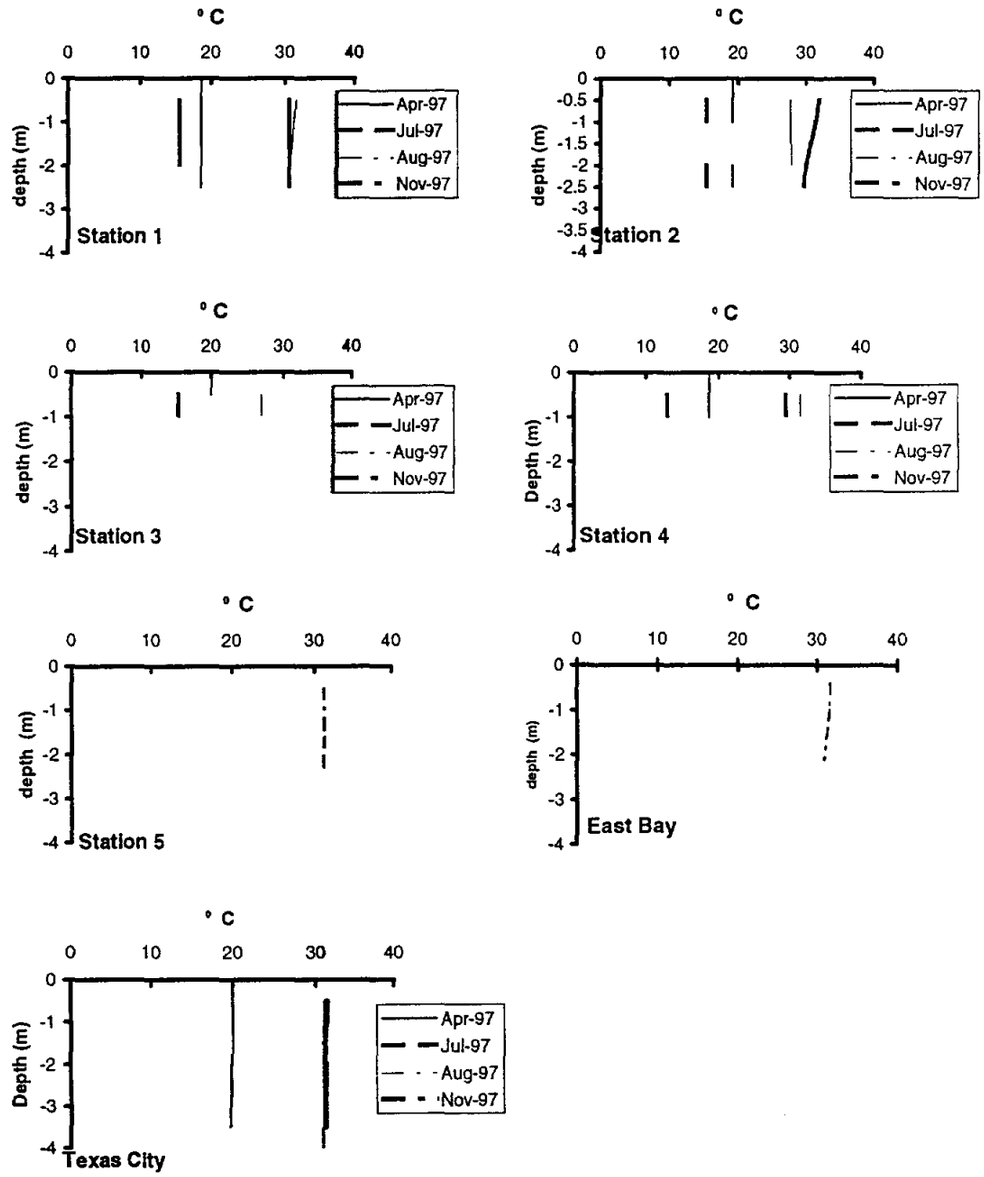

Figure 3. Temperature (^{0} C) versus depth during April, July, August, and November 1997 at all stations.

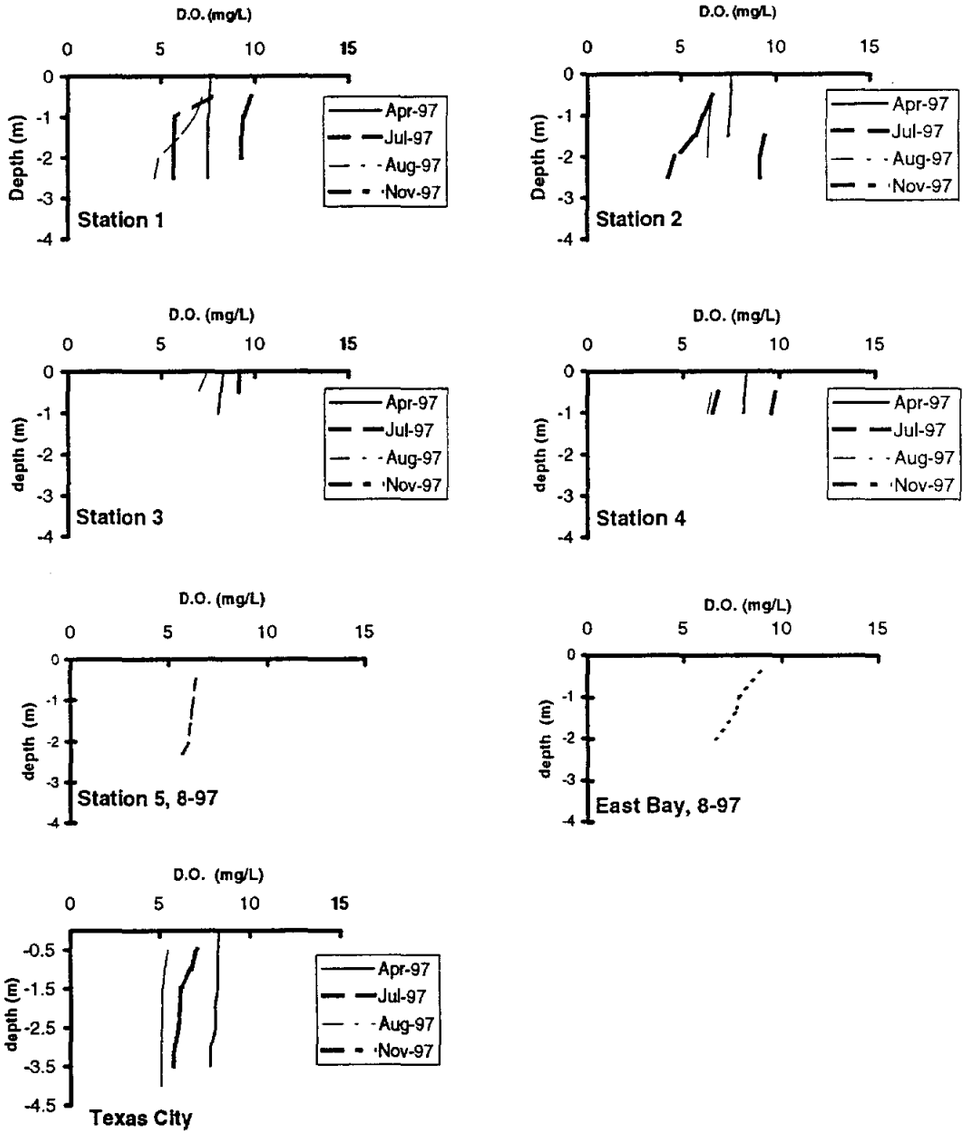

Figure 4. Dissolved oxygen (D. O.) versus depth during April, July, August and November 1997 at all stations.

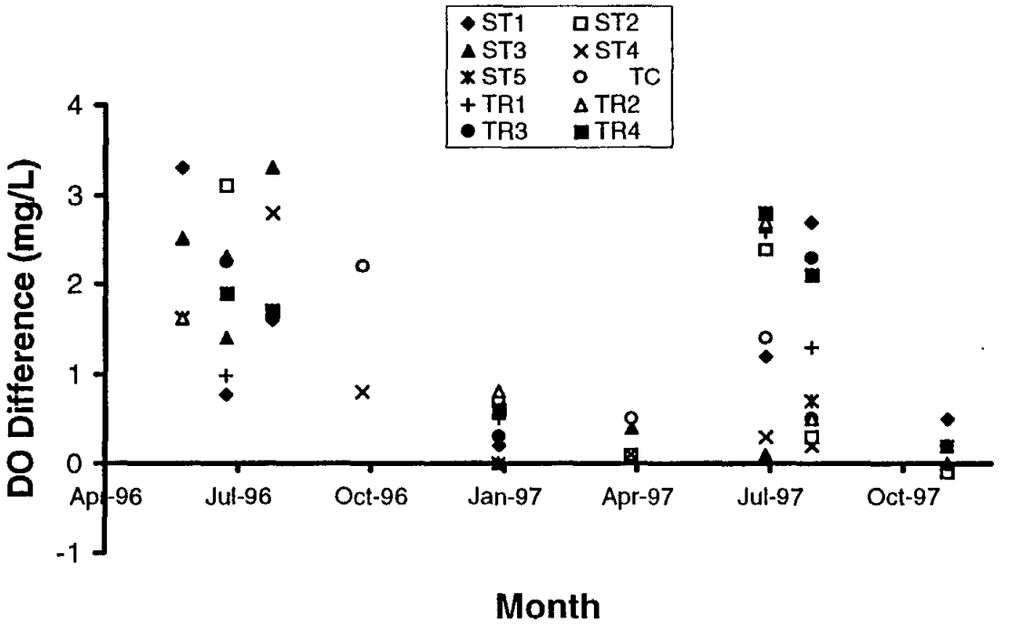

Figure 5. Surface - bottom difference in dissolved O_2 concentration (mg L-1) at all stations during 1996 - 1997.

gradients even in the presence of modest thermal stratification. Salinity probably contributes to stratification and this variable is correlated with freshwater inflow (Fig. 6); periods of high inflow are reflected in salinity reductions. However, there is usually insignificant microstructure in the salinity profiles at the shallow Trinity stations (Table 1). There was a slight salinity gradient in the water column of the deeper Texas City station during July (0.67 ppt/meter), but not during August (Fig. 7). Though the temperature increased by 10 degrees between July and August, the surface-bottom salinity (and temperature) difference decreased as did the surface-bottom D. O. difference. Clearly, short-term and possibly small scale variability in winds, as well as inflow, influence water column mixing and thus the distribution of physico-chemical parameters. Nonetheless, only slight gradients in temperature and salinity were required to support dramatic gradients in D.O. concentration.

Water column nutrient, dissolved N_2 and DIC concentrations. Water column nutrient concentrations along the Trinity River salinity gradient exhibited temporal as well as spatial (surface - bottom) differences. Variations in nutrient and dissolved gas concentration are presented in contour plots, for the ease of viewing. However, we should add a word of caution because our data were collected at approximately 2 month (or greater) intervals, thus interpolations between the actual data points is roughly estimated at best. Certainly, short term (days to week) variability is not captured by this approach.

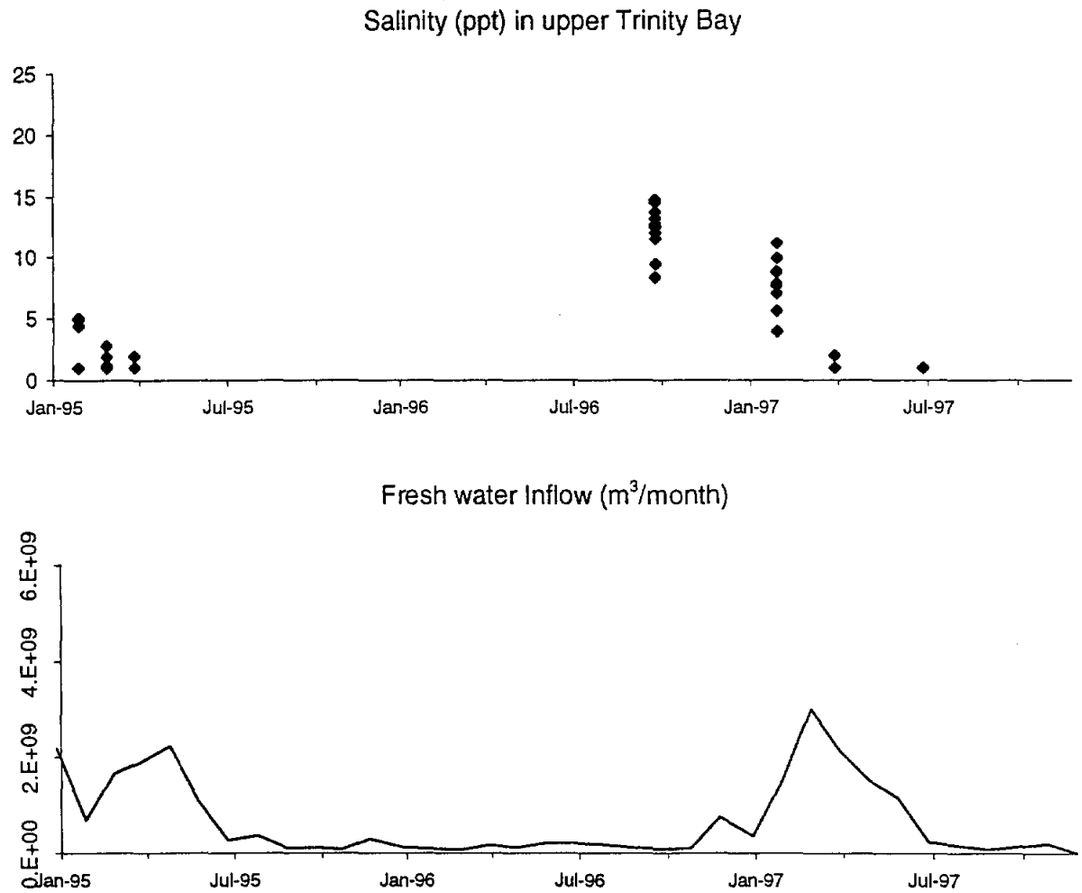

Figure 6. Salinity (ppt) in upper Trinity River and total freshwater input into Galveston Bay. Data from TNRCC (no salinity data are available for Jul-95 through Jul-96).

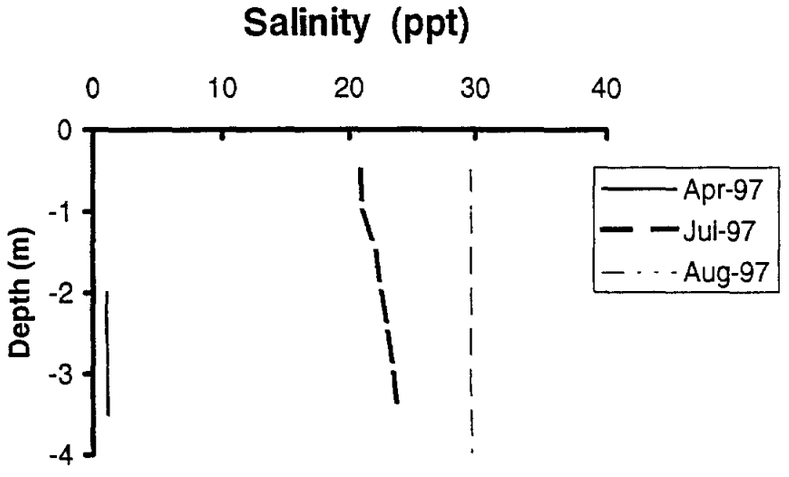

Figure 7. Salinity versus depth in the water column of the Texas City station.

Surface water ammonium concentrations were low (ca. 1 μM) throughout the year, with maximal values (2-4 μM) observed in the more saline regions during October-November (Fig. 8). Bottom water ammonium concentrations were significantly higher than surface water concentrations at all stations during 1996. Concentrations were as high as 10 μM were measured during 1996 but concentrations were low and consistent (around 1 μM) during 1997. This could be related to flow, since the freshwater inflow rate was much higher during 1997 than during 1996. This pattern could also reflect the end-member (freshwater) ammonium concentrations and the ammonium uptake rate (by phytoplankton) in the delta region. High flow rates, rapid exchange and enhanced uptake could contribute to and maintain the low standing concentrations in the delta region.

Oddly, dissolved phosphate concentrations did not exhibit as much variability between 1996 and 1997 (Fig. 9). Concentrations in surface waters were highest during late summer and fall in more saline waters (≥ Station 3). Surface-bottom water differences were greatest at the freshwater stations during 1996 (compared to 1997). Average concentrations in surface waters were approximately 3 μM during 1996 and 1 μM during 1997.

Water column nitrate (~nitrate + nitrite) concentrations typically exceeded ammonium concentrations with maximum concentrations observed during winter (Fig. 10). Maximal concentrations were 35 and 30 μM in surface and bottom waters,

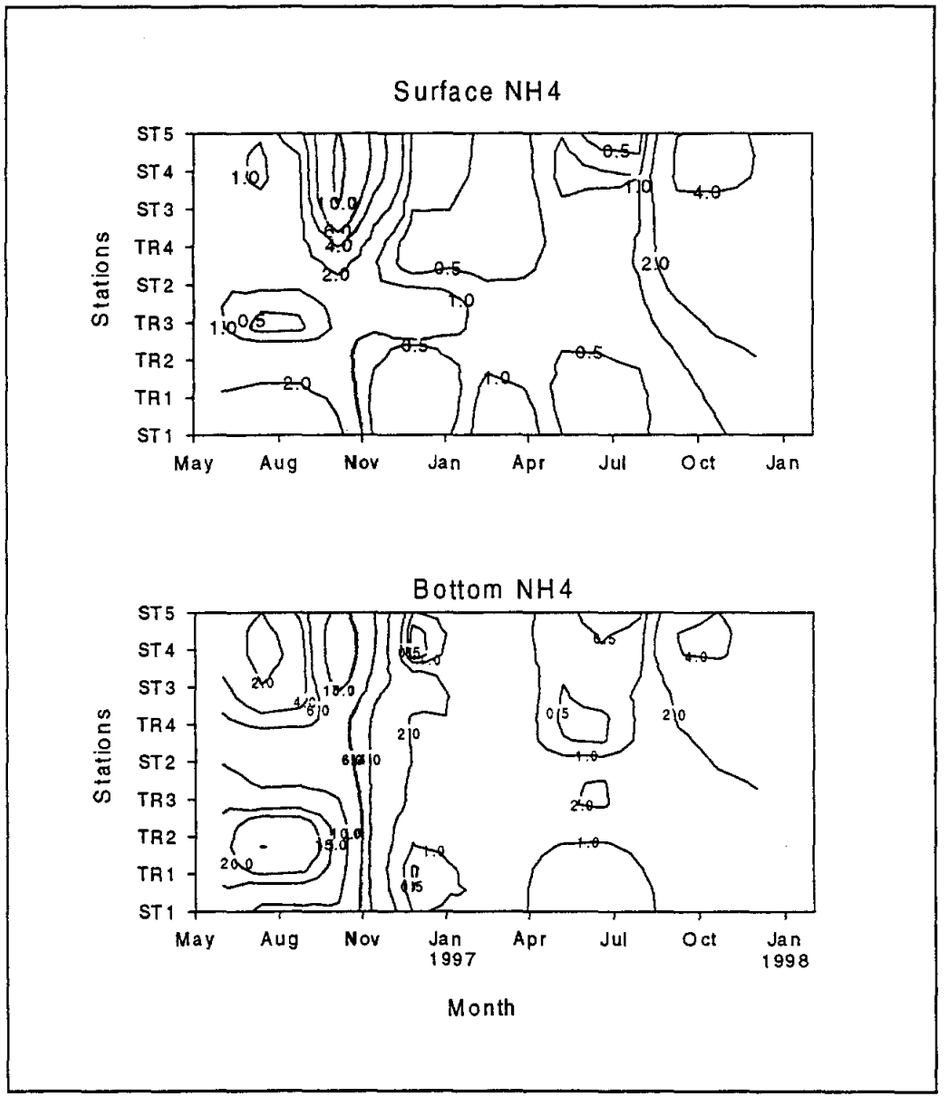

Figure 8. Surface and bottom water NH_4^+ concentrations (μM) the Trinity River region. Station 1 is located upstream while Station 5 is located at the edge of the delta in the Trinity Bay region (refer to Fig. 1b).

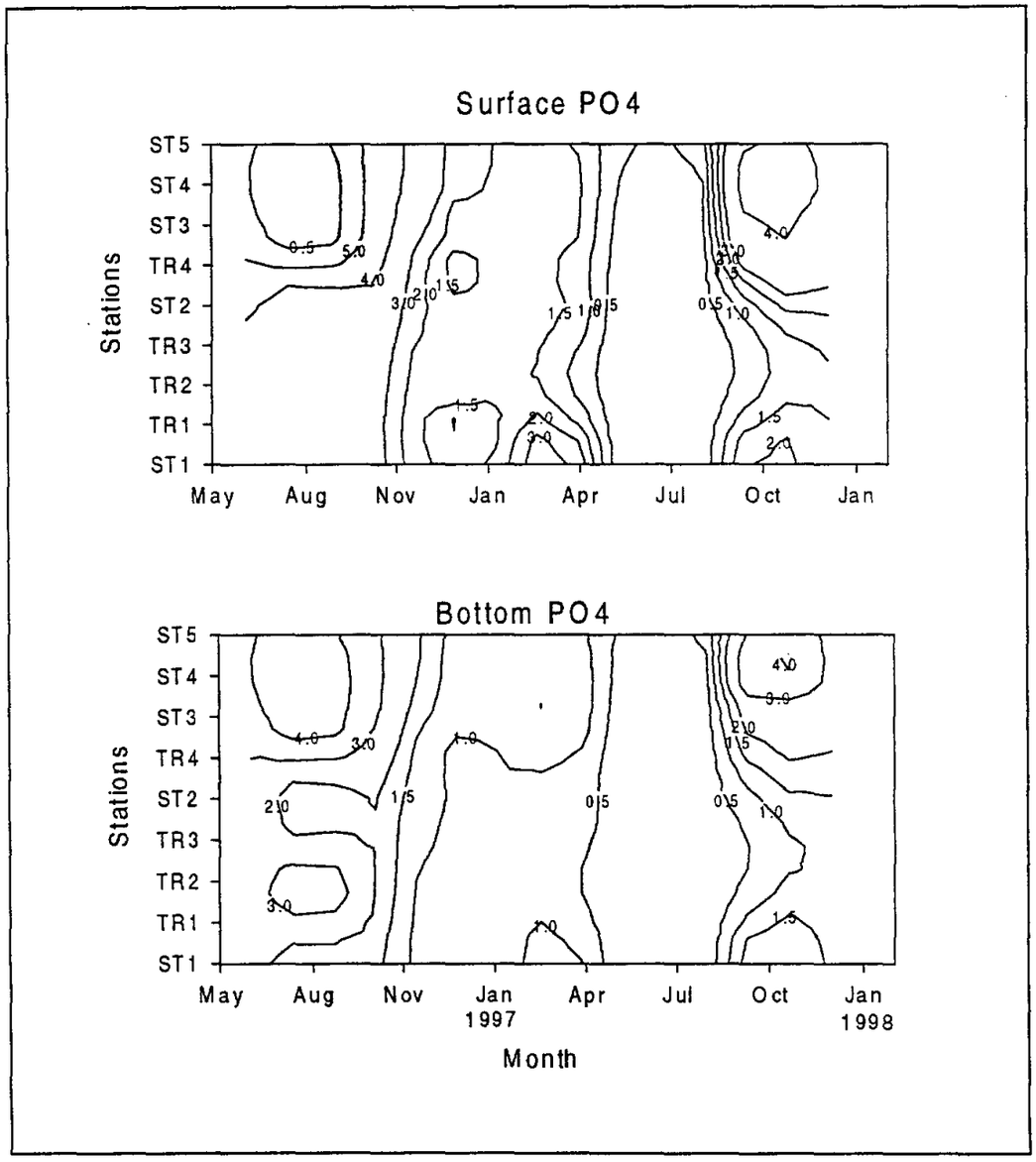

Figure 9. Surface and bottom water HPO_4^{2-} concentrations (μM) the Trinity River. Sampling stations same as noted on Fig. 8.

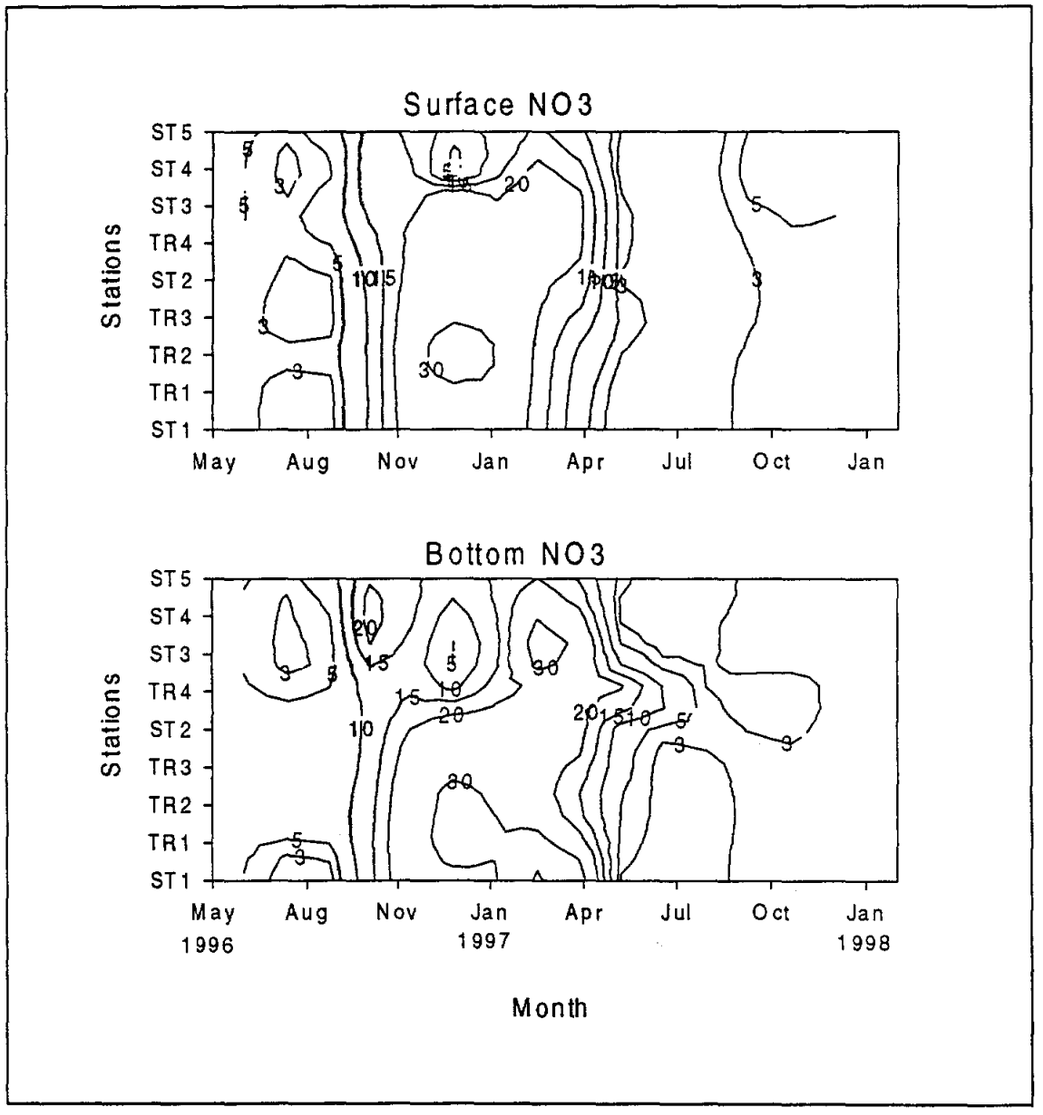

Figure 10. Surface and bottom water NO_3^- concentration (μM) the Trinity River. Sampling stations same as Figs. 8 & 9.

respectively. Concentrations during 1996 were similar to those observed during 1997. Lower concentrations in bottom waters may reflect uptake of nitrate via sediment denitrification. Water column N:P ratios suggest nitrogen limitation of primary production. If the data in figures 8-10 are compared, DIN (= nitrate + nitrite + ammonium) to DIP ratios of 7 and 9 are obtained for the surface waters during 1996 and 1997, respectively. Bottom water DIN:DIP ratios are 11 and 3 for 1996 and 1997 respectively. These ratios are well below the Redfield ratio of 16 and suggest an excess of inorganic P compared to inorganic N in Trinity Bay surface and bottom waters.

Spatio-temporal patterns in the distribution of DIC, dissolved N_2 and dissolved O_2 are presented in Figures 11-13. First, surface waters often exhibited higher DIC concentrations than did bottom waters at the more saline stations (Sta. 3 and 4). There was not a strong trend in DIC concentration along the salinity gradient; concentrations in the freshwater stations were approximately 1000 - 1400 μM while concentrations in the more saline stations were slightly higher, between 1400 - 1800 μM (Fig. 11). Decreased concentrations in bottom waters at stations 3 and 4 could be related to benthic production in shallow deltaic sediments (see below). Dissolved O_2 was always undersaturated in bottom waters (Fig. 12); whereas, dissolved N_2 % saturation exhibited no significant difference between surface and bottom waters over space or time (Fig. 13).

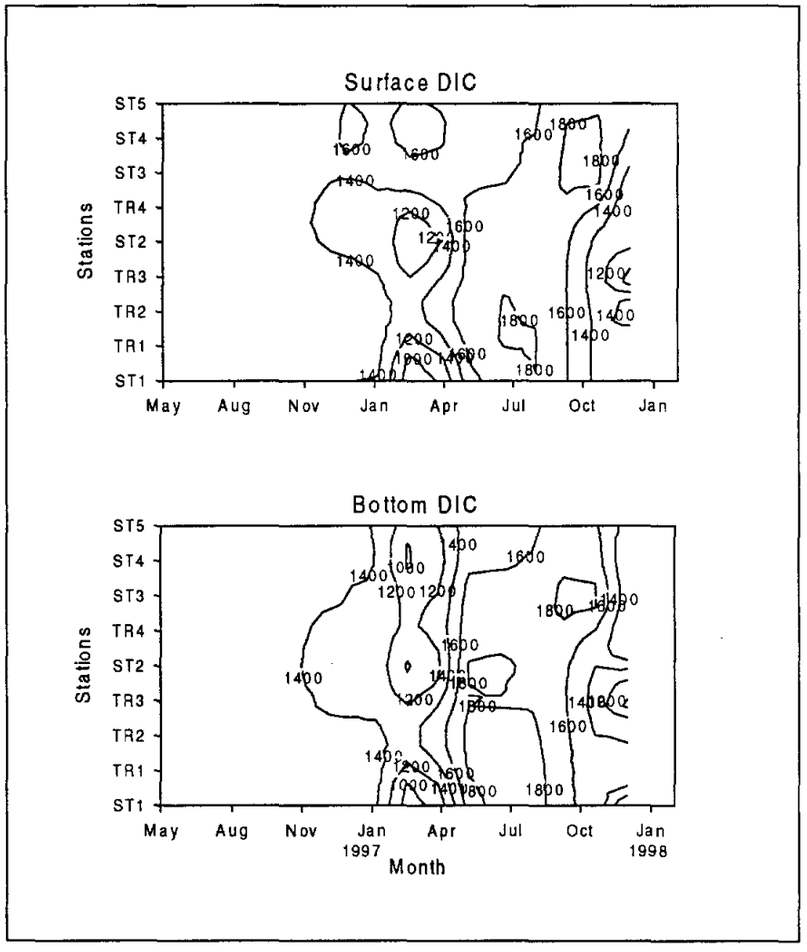

Figure 11. Surface and bottom water dissolved inorganic carbon (DIC) concentration (mM) along the Trinity River salinity gradient. Stations same as previous figures.

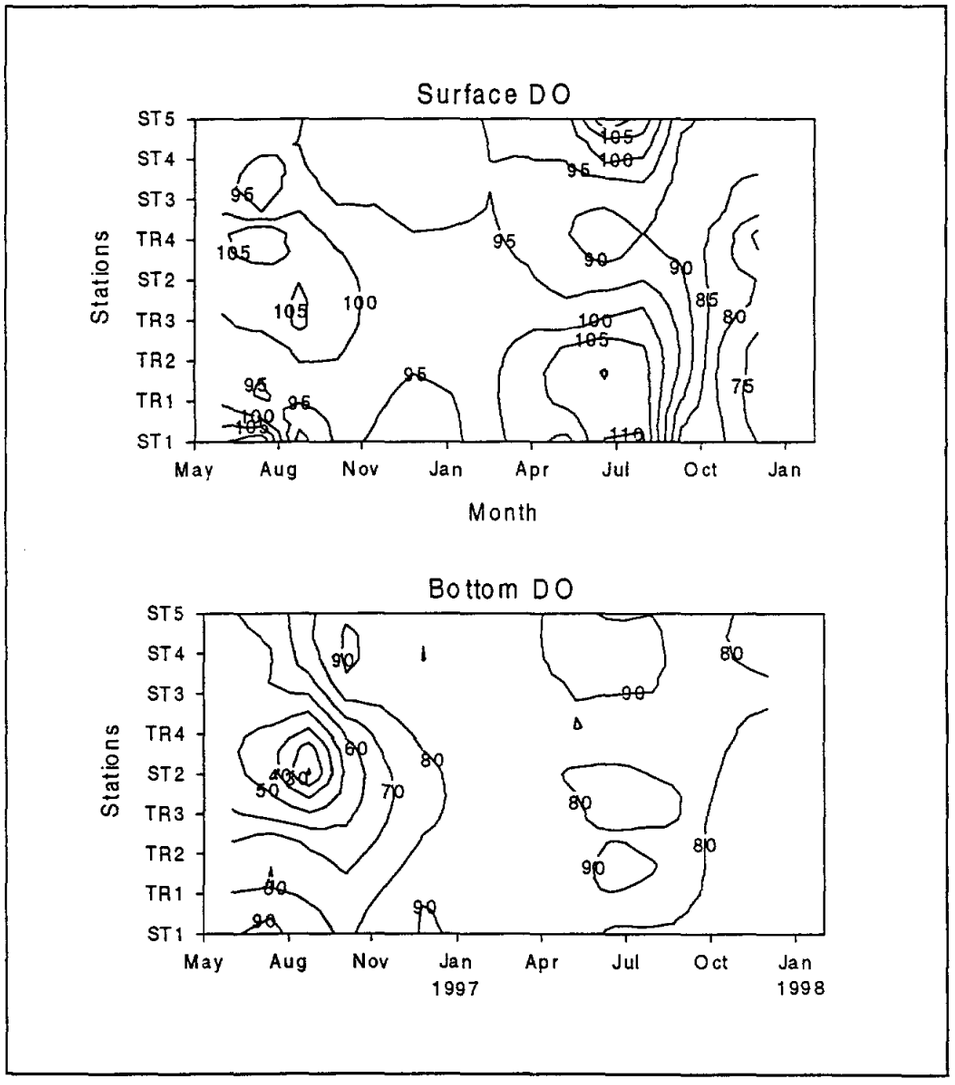

Figure 12. Percent saturation of dissolved O_2 in surface and bottom water along the Trinity river. Stations same as previous figures.

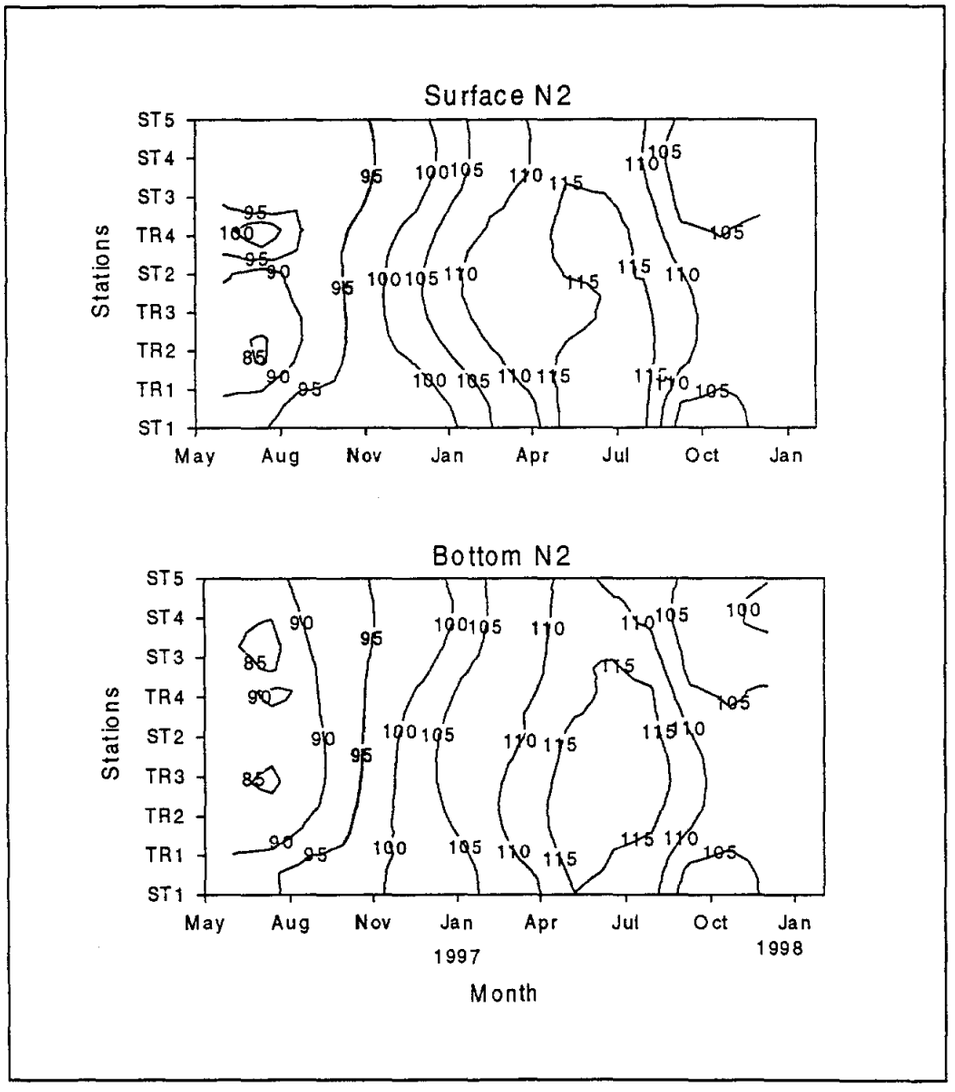

Figure 13. Percent saturation of dissolved N_2 in surface and bottom water along the Trinity river. Stations same as previous figures.

At the Texas City station, DIN concentrations were typically below 2 μM (Table 2). Only during April of 1997 were DIN concentration elevated (19 μM). Bottom water DIN concentrations were sometimes higher than surface water concentrations suggesting a benthic source for nitrate. Dissolved inorganic phosphate concentrations were low, frequently below detection. In contrast to the Trinity Delta, the DIN:DIP ratios in Texas City surface and bottom waters suggest N limitation during August 1996 and January 1997 but P limitation in April, July and August of 1997. Dissolved gas concentrations in Texas City waters exhibited surface-bottom differences in D.O., with surface water concentrations typically exceeding bottom water concentrations. DIC concentrations in bottom waters were higher but the differences were small and usually not significant. Similarly, there was no significant difference in dissolved N_2 concentration between surface and bottom samples (Table 2).

Pore water nutrient concentrations. Contour plots of pore water ammonium, nitrate and phosphate concentrations at all stations throughout the study period are shown in Figures 14-20. In the freshwater stations, pore water ammonium concentrations were low and increased only slightly with depth during summer (ca. 60 μM at the surface to 120 μM at 20 cm). During winter, concentrations increased but overall ammonium concentrations were lowest in the porewaters of Stations 1 and 2 (Fig. 14 & 15). Pore water nitrate concentrations were high, reaching 30 μM during summer (1997). Both surface and mid-depth peaks of nitrate+nitrite were observed in Sta. 1 pore

Table 2. Surface and bottom water concentrations of dissolved gases and nutrients at Texas City. All concentrations are in µM and n. d. = No data.

	Aug-96		Jan-97		Apr-97		Jul-97		Aug-97	
	surface	bottom	surface	bottom	surface	bottom	surface	bottom	surface	bottom
Gas										
N_2	411	392	537	488	563	549	**n.d.**	457	440	446
O_2	221	197	284	257	**n.d.**	**n.d.**	**n.d.**	209	248	199
DIC	**n.d.**	**n.d.**	1654	1834	1709	1763	2050	2090	2039	2226
Nutrient										
NH_4^+	0	0	0	0	0	1	1.1	2.1	0.7	0.5
NO_3^-	0.48	0.83	0.22	0.62	19.3	16.3	**n.d.**	0.19	**n.d.**	0.5
HPO_4^{2-}	1.2	0.98	0.53	0.3	0	0	0	0	0	0

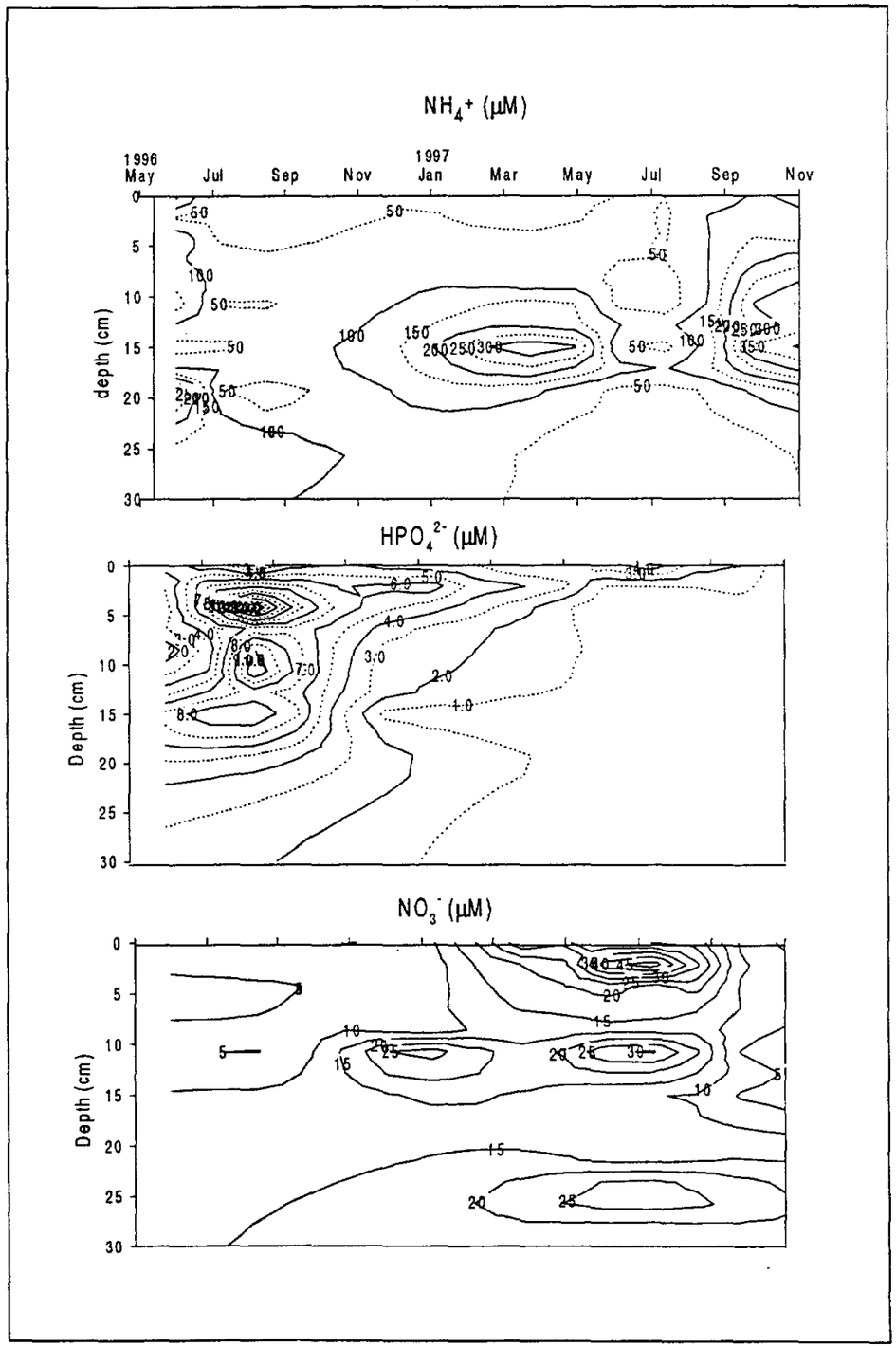

Figure 14. Station 1 pore water concentration (contours in µM) of NH_4^+, HPO_4^{2-}, and NO_3^- versus depth downcore in cm.

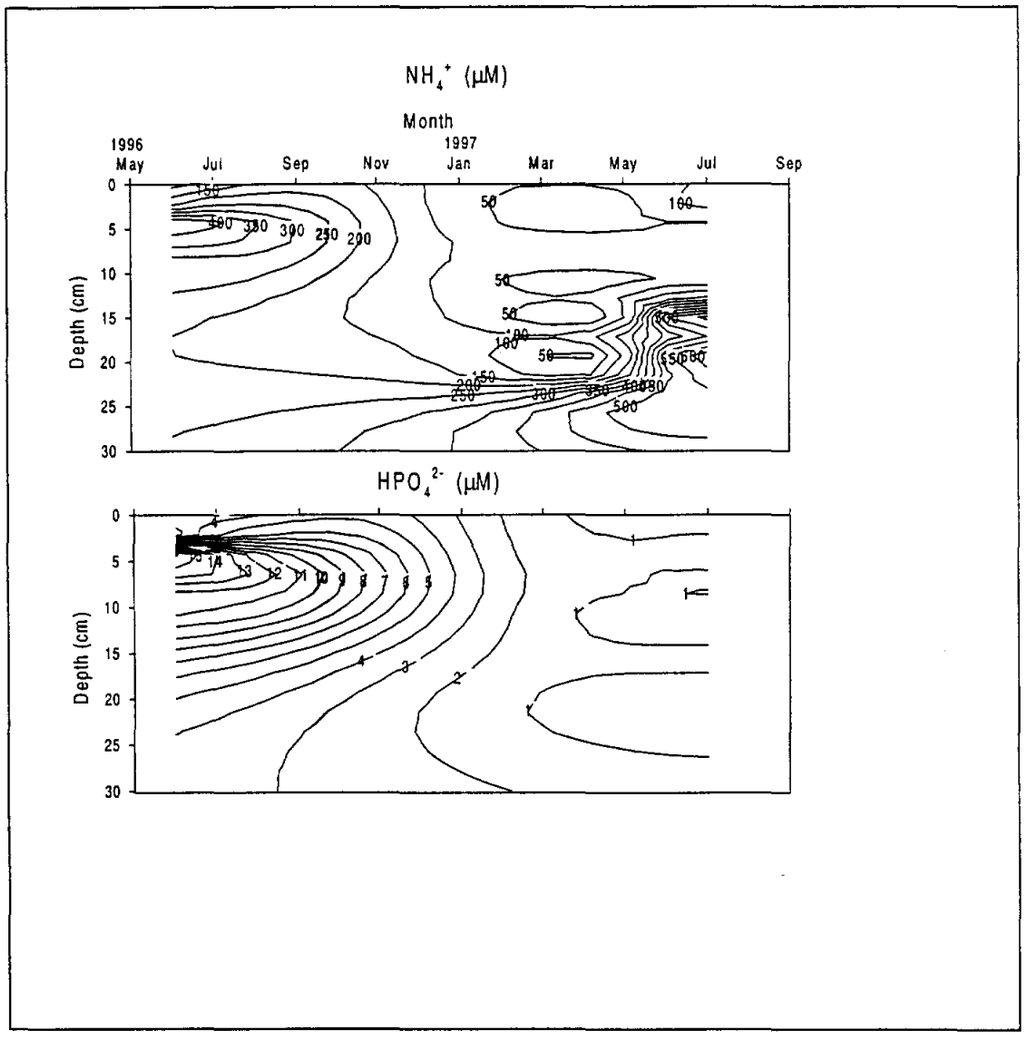

Figure 15. Station 2 pore water concentration (contours in µM) of NH_4^+, HPO_4^{2-}, and NO_3^- versus depth down core in cm.

waters (Fig. 14). We were unable to collect enough water from Sta. 2 to determine pore water nitrate concentrations. Dissolved inorganic phosphate concentrations were low at Station 1 (1.5 - 7 μM). There was an excess of DIP compared to DIN in 1996 (DIN:DIP ~ 13) in the upper 5 cm of sediment but a reversal of that pattern at depth (DIN:DIP ~ 26 at 20 cm). During 1997, pore waters were depleted with P and the pore water DIN:DIP ratio exceeded 200. Dissolved inorganic P participates in reversible sorption-desorption reactions in pore waters and it is likely that the low pore water DIP concentration results from the sorption of P onto solid phase Fe-oxyhydroxides. The lack of a summer build up of DIP in porewaters at Stations 1 and 2 suggests that these sediments remain relatively oxidized during summer and that Fe-oxyhydroxides are not reductively dissolved (which would lead to increased pore water inventories of DIP; Fig. 14 & 15).

Pore water nutrient concentrations increased further down the Trinity salinity gradient. At station 3, ammonium concentrations exhibited a mid-depth maximum (~300 μM at ca. 15 cm). During summer, increased concentrations were observed over a broad depth range (Fig. 16). Nitrate was abundant in these sediments suggesting active mixing with bottom waters and/or in situ nitrification. Bottom water concentrations were typically higher than pore water concentrations during winter but not during summer (Fig. 10 & 16). This pattern suggests that *in situ* nitrification produces the excess pore water nitrate observed during summer, while mixing alone could explain the winter pore water concentrations. For example, if bottom water

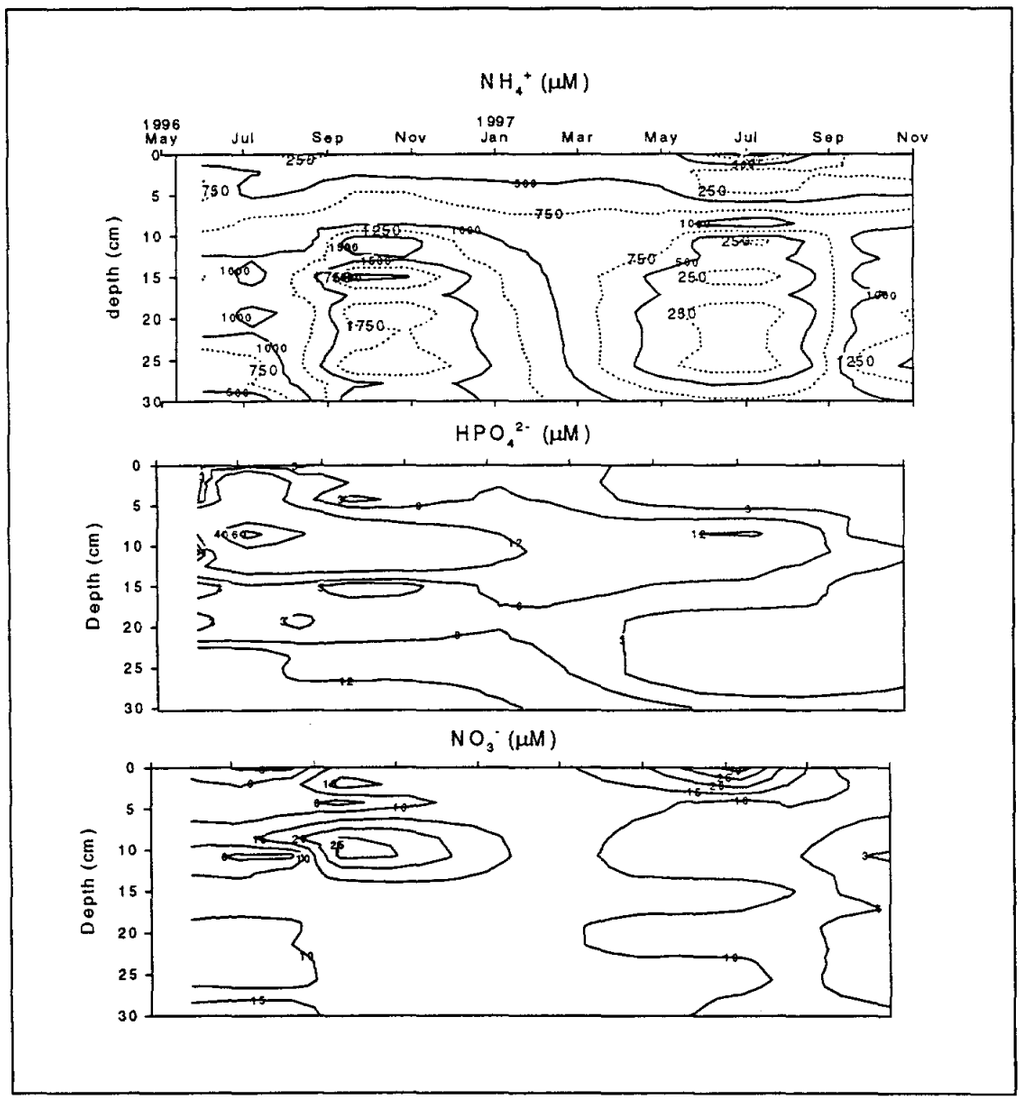

Figure 16. Station 3 pore water concentration (contours in μM) of NH_4^+, HPO_4^{2-}, and NO_3^- versus depth down core in cm.

concentrations exceed pore water concentrations, then mixing of bottom water with sediment pore water could supply nitrate to the sediment. However, if pore water concentrations exceed those in the overlying water, then there must be an internal source. If bottom water concentrations are lower than pore water concentrations, then their mixing would dilute, not increase, the pore water concentration. This is particularly obvious during the summer of 1997 when sharp pore water nitrate+nitrite gradients were observed in the upper 5 cm; pore water concentrations were three times higher than the bottom water concentrations. Dissolved inorganic phosphorus concentrations were higher during 1996 and were low, and relatively uniform throughout 1997 (Fig. 16).

Station 4 pore waters consistently exhibited the highest concentrations of ammonium. Concentrations were maximal during summer and increased with depth (Fig. 17). Dissolved inorganic phosphate concentrations were also highest at this station, with concentrations up to 30 μM observed during spring and early summer. Pore water nitrate concentrations were elevated during spring and early summer and exhibited a bi-modal distribution, with surface and mid-depth maxima. At Station 5, ammonium concentrations increased linearly over the upper 10 cm. Nitrate concentrations were ca. 8 μM in the surface sediments and exhibited a striking peak at depth in the sediment column (Fig. 18). Phosphate concentrations were beneath the detection limit throughout most of the sediment column.

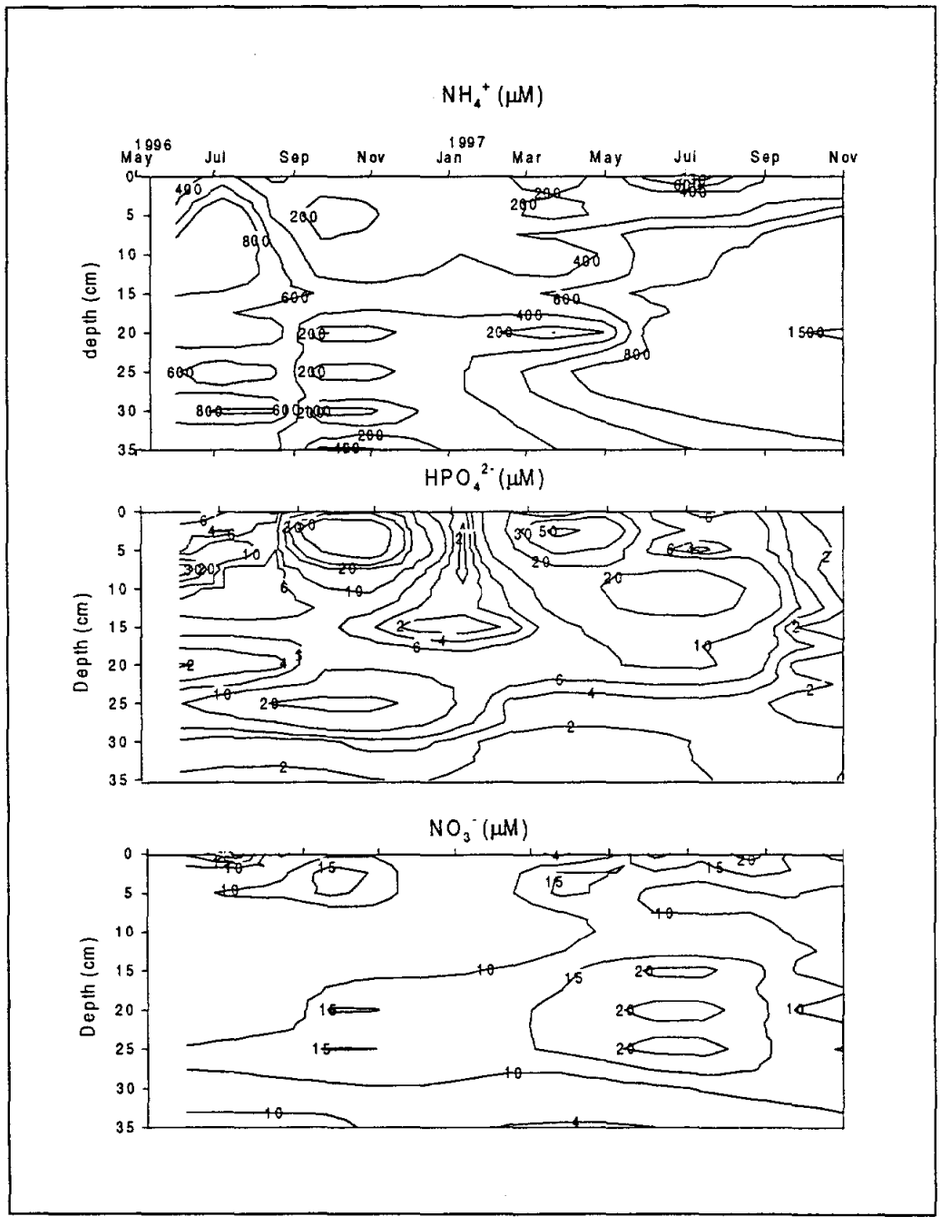

Figure 17. Station 4 pore water concentration (contours in μM) of NH_4^+, HPO_4^{2-}, and NO_3^- versus depth downcore in cm.

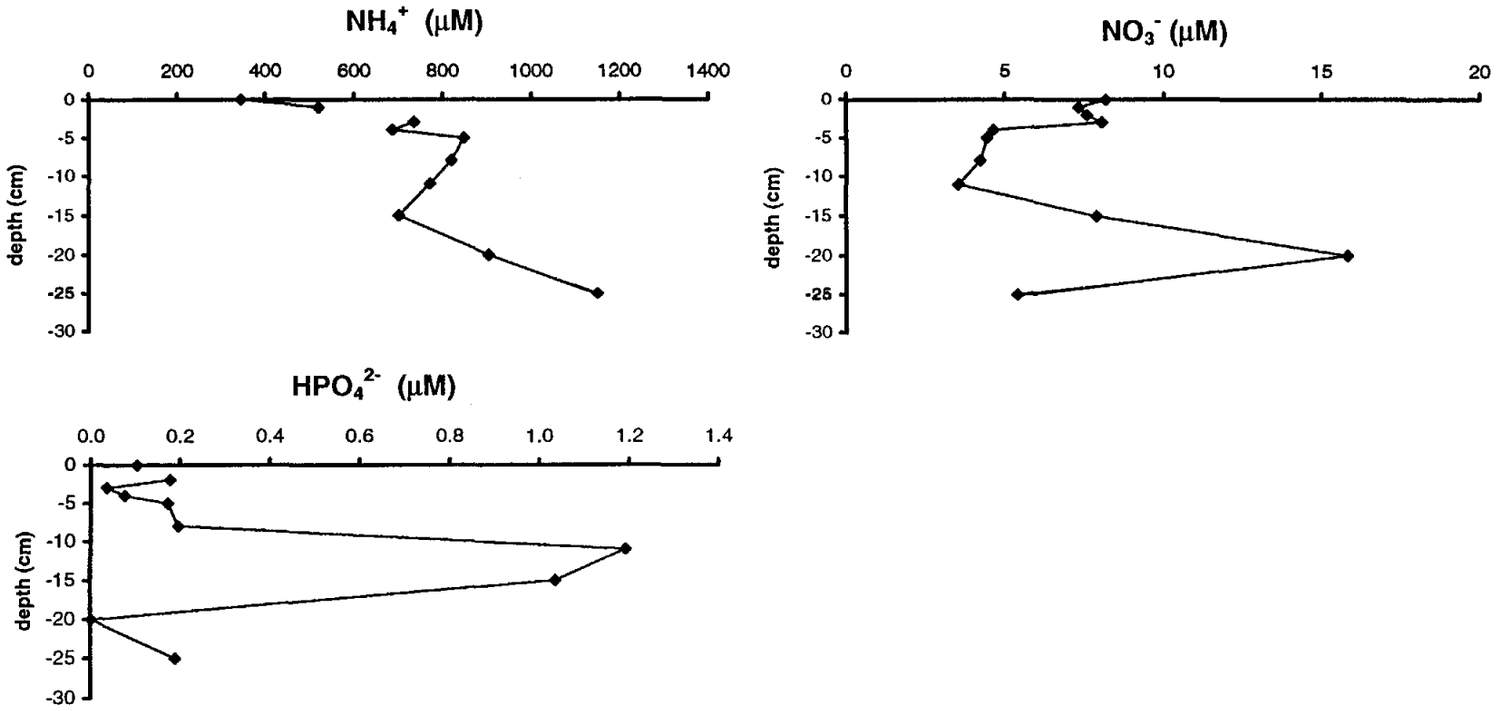

Figure 18. Station 5 pore water concentrations (μM) of NH_4^+, HPO_4^{2-}, and NO_3^- versus depth downcore in cm (Aug. 1997 data only).

Texas City pore water ammonium concentrations were low during 1996 but exhibited a seasonal build up of ammonium from January to August of 1997 (Fig. 19). Concentrations tended to increase slightly with depth. Nitrate concentrations in these sediments followed a bi-modal distribution during spring and summer with highest in the upper 5 cm and between 20-25 cm. Phosphate concentrations were low, and as observed in the Trinity River sediment porewaters, DIN:DIP ratios were high (710:1.7 ~ 350) suggesting an excess of N relative to P in porewaters.

The East Bay station pore waters had low ammonium concentrations in the upper few cm; this region had high nitrate concentrations (Fig. 20). When ammonium concentrations increased, nitrate concentrations decreased. Phosphate concentrations peaked at the same depth where nitrate decreased and ammonium began to increase, suggesting a strong redox boundary at ca. 4 cm.

Grain Size. Part of the variability in pore water concentration is related to differences in sediment grain size and sedimentation rate. Trinity stations 1 & 2 and Texas City sediments were predominately sands (≥ 80% of sediment greater than 63 μm; Fig. 21). Stations 3 and 4 in the Trinity and the East Bay station were muddy sands. Station 4 sediments were unique in that there was a muddy regions in between two sandy lens. Grain size distribution in surface sediments was relatively constant at Texas City but varied quite a bit at Trinity Stations 3 & 4 (Fig. 22).

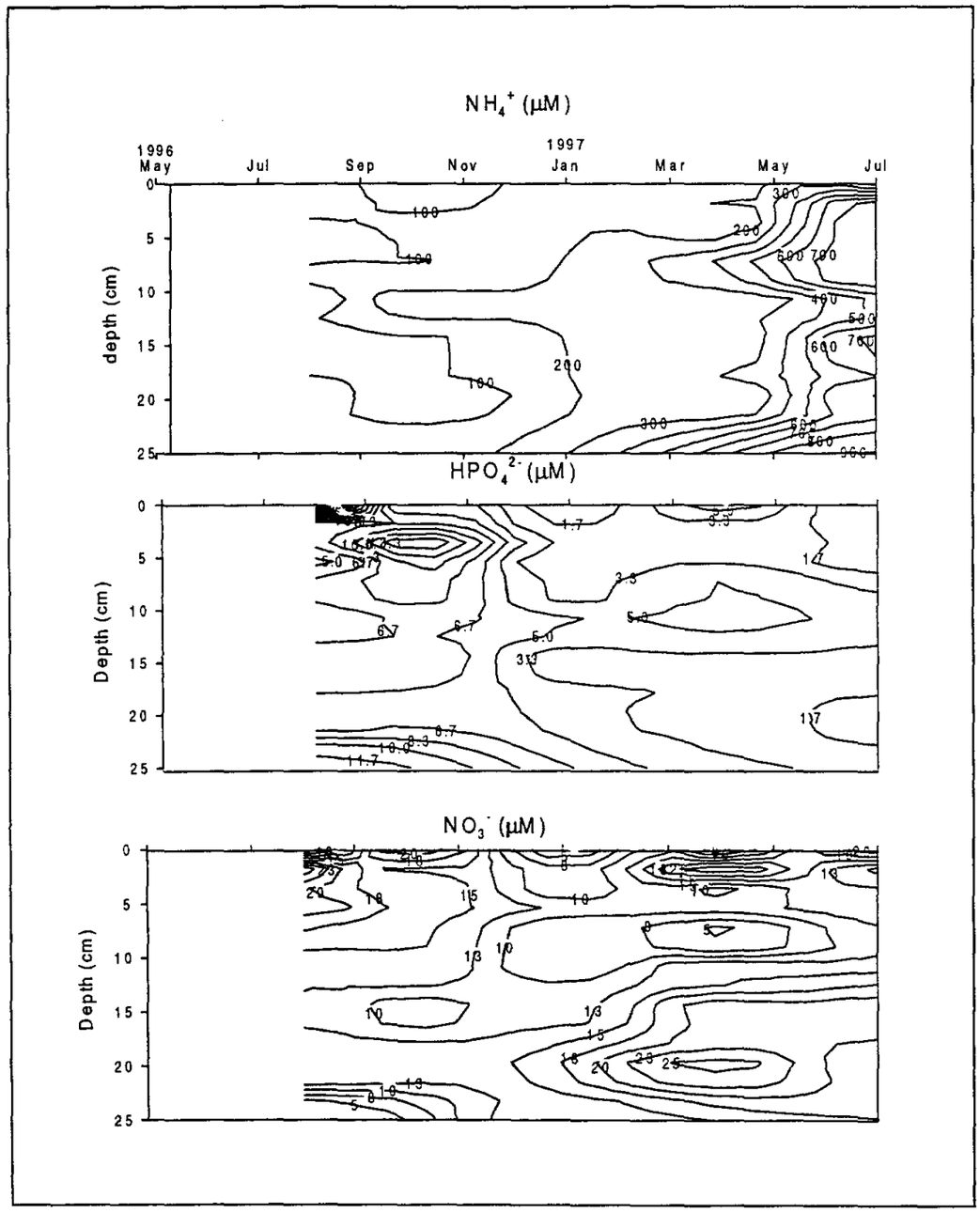

Figure 19. Texas City pore water concentration (contours in μM) of NH_4^+, HPO_4^{2-}, and NO^{3-} versus depth downcore in cm.

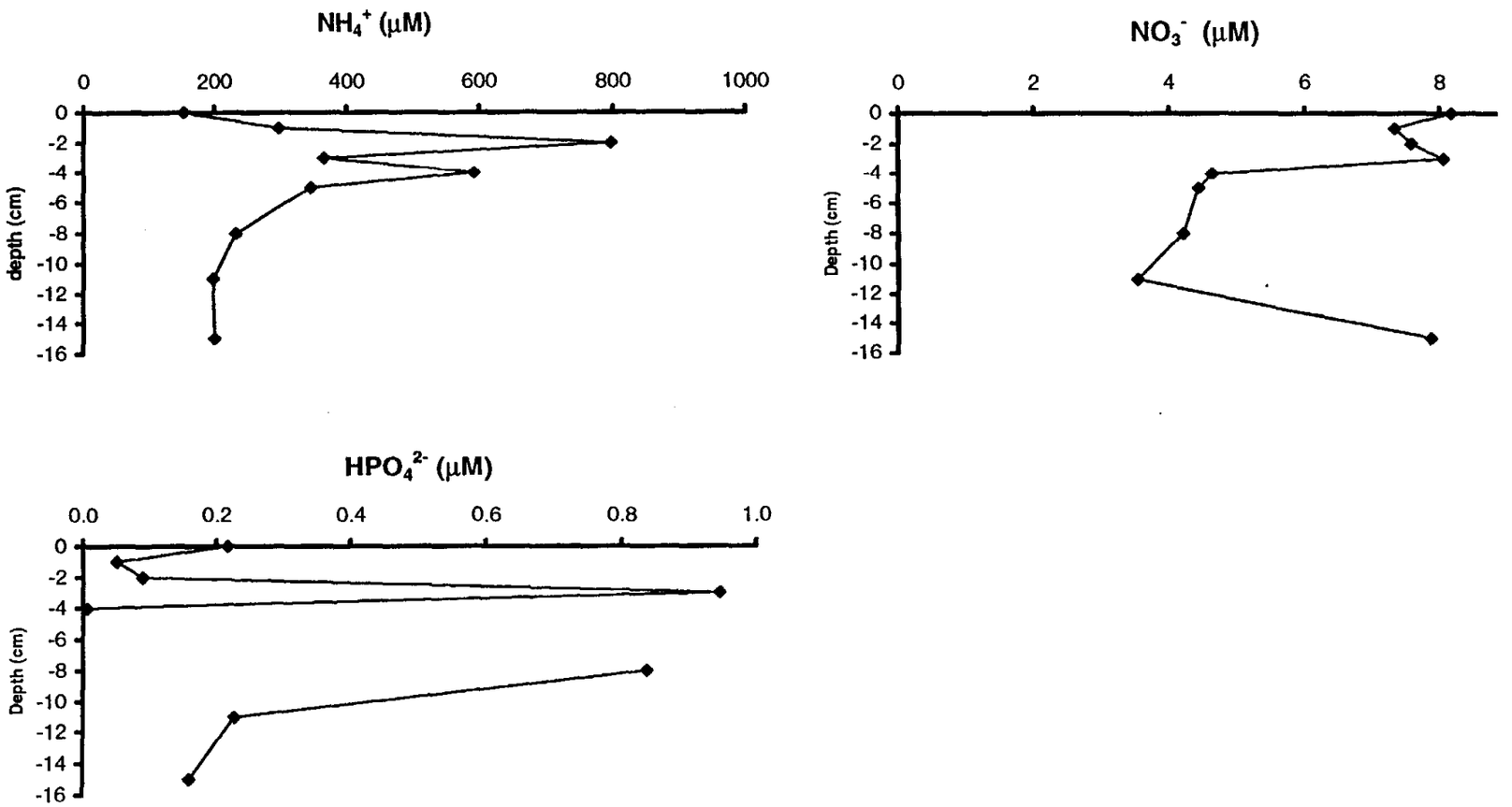

Figure 20. East Bay pore water concentration (μM) of NH_4^+, HPO_4^{2-}, and NO_3^- (data from Aug. 1997 only).

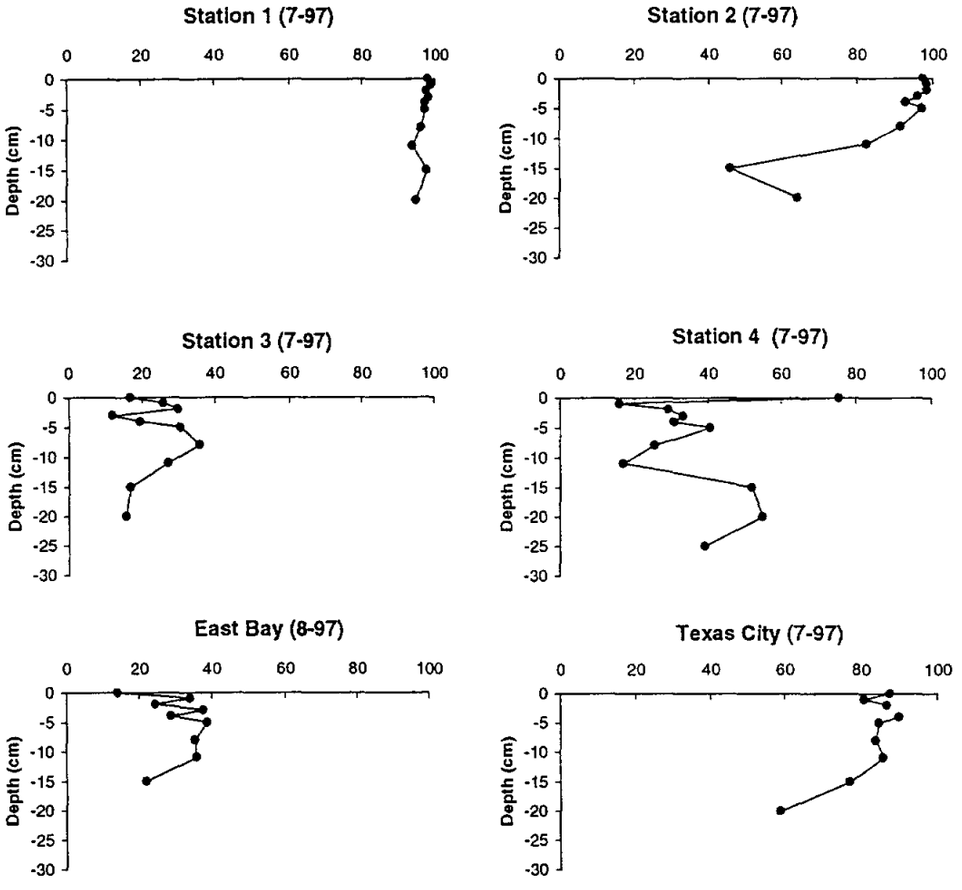

Figure 21. Variability in % sand (~ % > 64 µm) over depth in Galveston bay sediments during July and August of 1997.

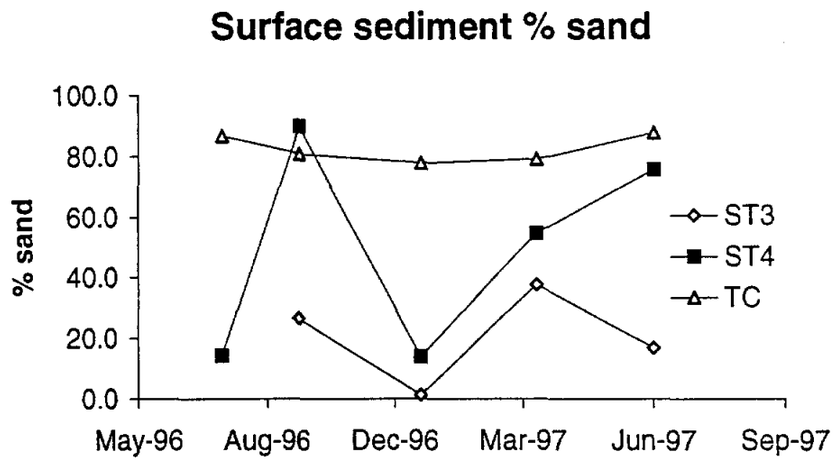

Figure 22. Percent sand (~ % greater than 64 μm) in the top cm of sediments in Stations 3, 4 and Texas City at selected time points during 1996 & 1997.

Benthic Chlorophyll. Benthic chlorolhyll *a* concentrations were determined at all stations during 1997 and on samples from 1996 when frozen archival samples were available. Chlorophyll *a* concentrations were high, up to 1000 mg Chl m^{-2} of sediment at Station 4 and in the East bay. Concentrations at Texas City were ca. 200 mg Chl *a* m^{-2} throughout the year (Fig. 23). There was no obvious correlation between bottom water O_2 concentration and sediment chlorophyll distribution (Fig. 23). As expected, chlorophyll concentrations were highest in surface sediments although sub-surface peaks were observed on occasion (Fig. 24). The highest concentrations per volume of sediment were observed at the East Bay, Trinity Station 3, and Texas City stations. Benthic chlorophyll concentrations reported here are similar to those reported other coastal aquatic ecosystems (Joye et al. 1996; Pind et al. 1997). The abundance of chlorophyll suggests that benthic primary production is important in this system.

Benthic fluxes. Denitrification rates, the sediment DIC flux, and the sediment oxygen demand (SOD) exhibited similar seasonal and interannual variation (Fig. 25). Sediment denitrification rates were highest during summer and maximum rates were observed at the Station 5 in the Trinity and in the East Bay station. The denitrification rates observed during the summer of 1996 and 1997 were similar. The highest denitrification rates occurred when N loading rates were at a minimum (Fig. 25). DIC fluxes and the SOD followed a similar seasonal pattern, with highest fluxes observed during summer (Fig. 25). The benthic DIC flux exhibited much more spatio-temporal

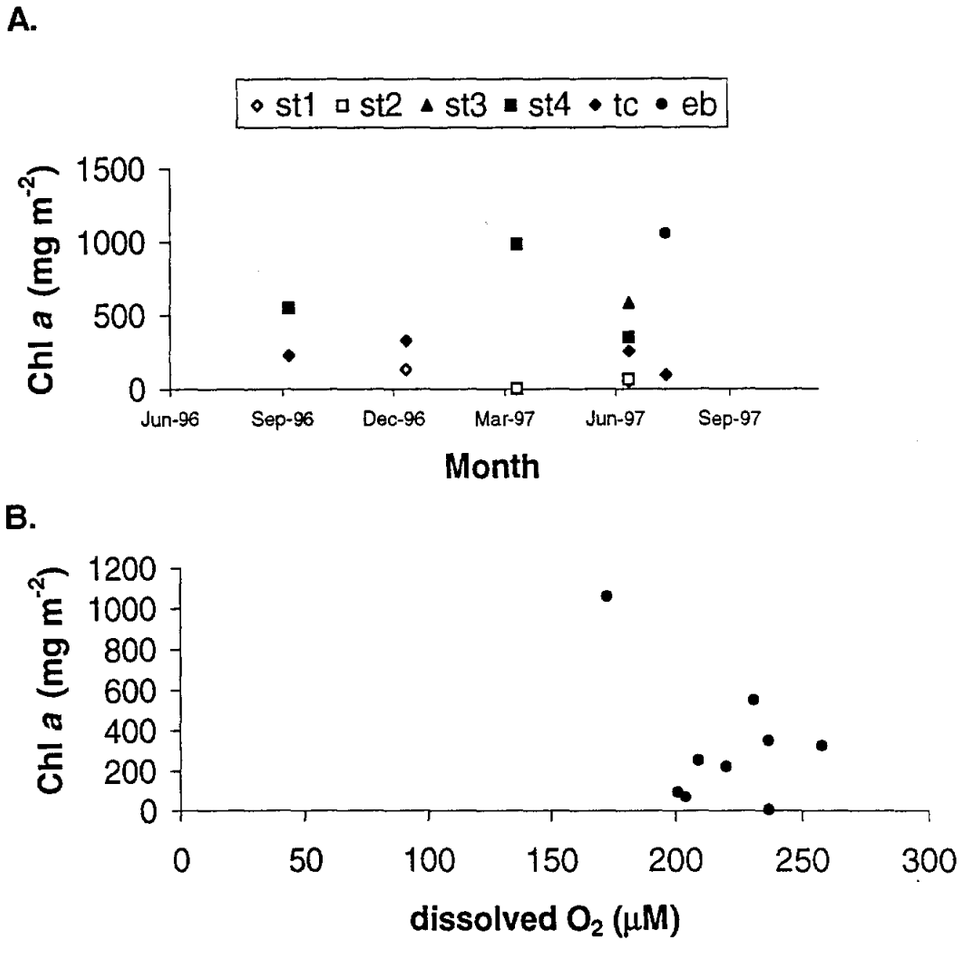

Figure 23. Chlorophyll *a* concentration (mg m^{-2}) of surface sediment by month (A) and plotted against bottom water O_2 concentration (B). In panel A, st1-4 refers to the Trinity River station number, tc = Texas City, and eb = East Bay.

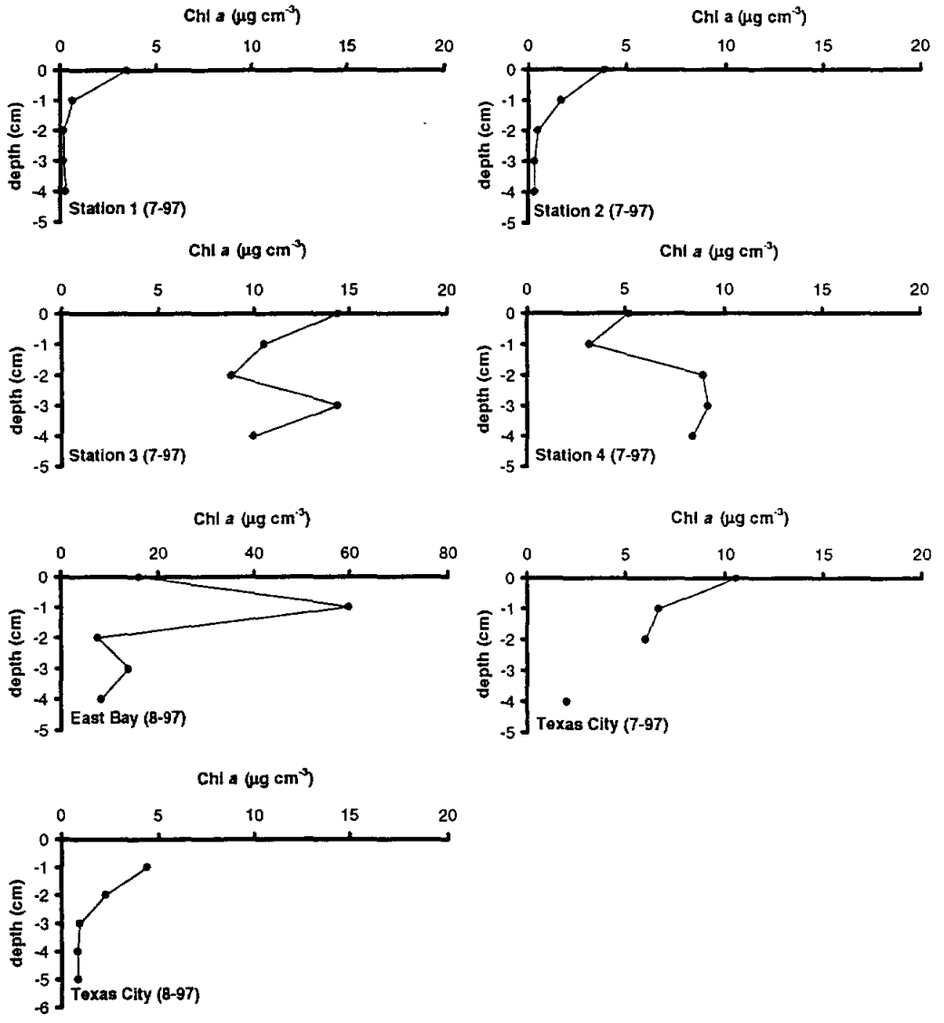

Figure 24. Chlorophyll *a* concentration (µg cm^{-3}) versus depth downcore (cm) in Galveston Bay sediments during July and August of 1997. Note the expanded scale on the East Bay panel.

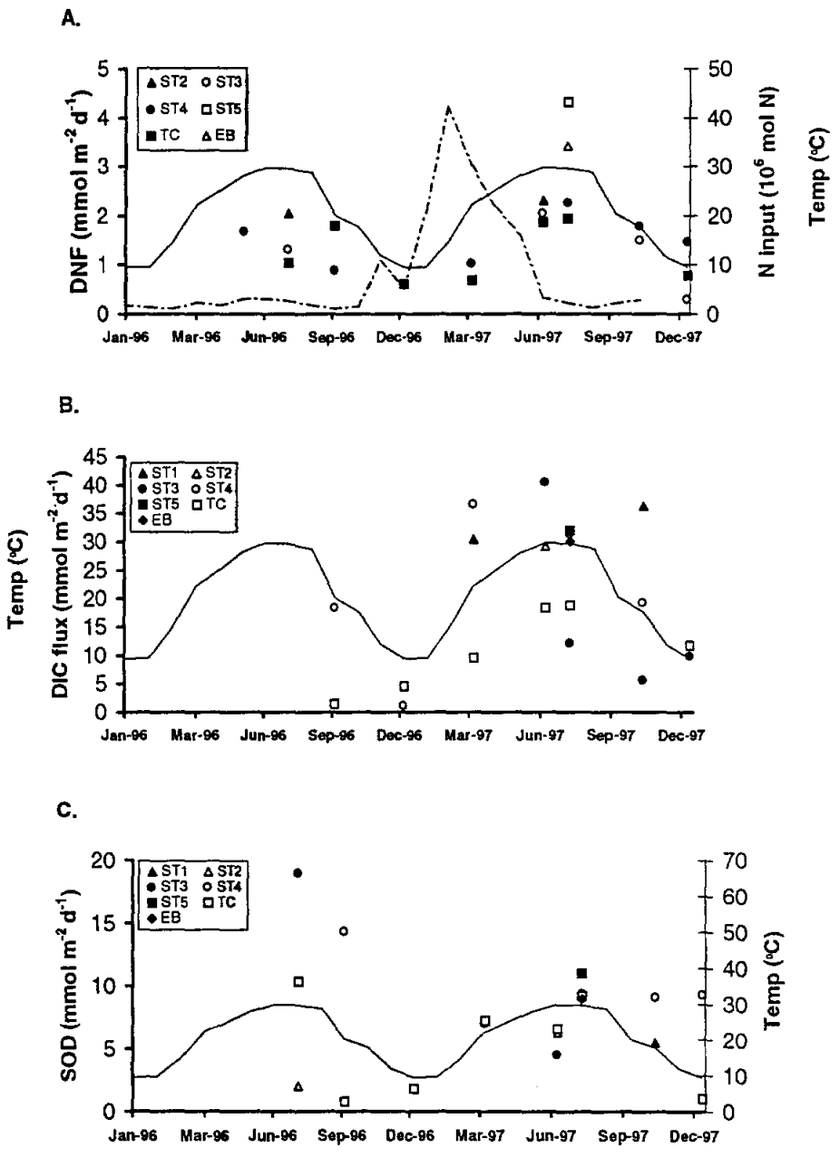

Figure 25. Variation over time of denitrification (data points), N loading (dotted line), and temperature (solid line) (A); DIC flux (data points) and temperature (solid line) (B); and sediment oxygen demand (SOD) (data points) and temperature (solid line) (C). Refer to legends for site identification.

variation than did denitrification rates. Inter-site differences in the SOD were similarly variable.

Benthic fluxes of dissolved gases, DIC, and nutrients are presented in Table 3. For dissolved inorganic nutrients, observed fluxes were measured in benthic chambers while calculated fluxes were estimated using a non-linear fitting routing (Joye and An 1997). Positive fluxes denote a flux from the sediment to the water column while a negative flux denotes a flux from the water column to the sediment. Ammonium fluxes were usually positive, except during August 1996, when substantial ammonium uptake was documented at Station 3. At the Texas City station, ammonium fluxes were positive, but typically well below 1 mmol N m^{-2} d^{-1}. Nitrate fluxes were generally negative in the Trinity freshwater stations and either slightly positive or not measurable at the other stations. Dissolved inorganic phosphorus fluxes were generally small and positive. However, on one occasion, a large, negative flux of DIP was observed at Station 3 (July 1997; Table 3). Generally speaking, the sediments were a small source of DIN and a sink for DIP. Given the patterns observed for water column dissolved nutrient distribution, this was to be expected.

The ratio of the benthic fluxes of DIC to the SOD (i.e., the amount of DIC produced per unit of O_2 consumed) in Galveston Bay sediments varies between 1 and 10. This ratio of the DIC flux divided by the SOD is referred to as the respiration

Table 3. Dissolved gas and nutrient fluxes from Glaveston Bay, Texas, sediments.
All units are mmol m^{-2} d^{-1}; **n.d.** = no data.

Station	ST1		ST2		ST3					ST4			
month	Apr-97	Nov-97	Aug-96	Jul-97	Aug-96	Jul-97	Aug-97	Nov-97	Jan-98	Jun-96	Oct-96	Jan-97	Apr-97
Dissolved gases													
N_2	6.1	4.6	2.0	2.3	1.3	2.0	**n. d.**	3.9	0.3	1.7	0.9	0.6	1.0
O_2	**n. d.**	-5.5	-2.0	-6.3	-19.0	-4.5	7.4	15.9	1.7	**n. d.**	-20.2	-2.0	-7.1
DIC	30.4	36.3	**n. d.**	29.2	**n. d.**	40.5	12.1	5.6	9.9	**n. d.**	19.0	1.2	36.6
Nutrients													
NH_4^+	-0.19	2.25	2.97	**n. d.**	-1.83	0.14	0.49	-0.12	-0.12	**n. d.**	0.64	0.03	-0.05
NO_3^-	2.60	-0.48	-0.25	-0.02	-0.17	-0.13	0.14	-0.14	-0.64	**n. d.**	-0.09	0.01	-1.12
HPO_4^{2-}	0.03	0.44	0.22	**n. d.**	-0.40	-0.02	-0.01	-0.15	**n. d.**	**n. d.**	-0.19	0.00	0.00

Station	ST4			ST5	Texas City								East Bay
month	Aug-97	Nov-97	Jan-98	Aug-97	Aug-97	Aug-96	Oct-96	Jan-97	Apr-97	Jul-97	Aug-97	Jan-98	Aug-97
Dissolved gases													
N_2	2.3	1.8	1.5	3.3	5.4	1.0	2.6	0.6	0.7	1.9	1.9	0.8	2.8
O_2	-9.4	-9.1	-9.3	-11.6	-10.6	-10.4	-2.0	-1.8	-7.3	-6.6	-9.2	-1.0	-8.5
DIC	31.4	19.3		26.9	38.7		3.0	4.5	9.6	18.4	18.8	11.7	25.4
Nutrients													
NH_4^+	0.43	1.58	**n. d.**	0.55	1.55	0.28	-0.55	-0.05	-0.05	0.94	0.82	**n. d.**	1.45
NO_3^-	0.14	0.13	-0.64	**n. d.**	0.95	0.04	0.01	-0.02	-0.02	0.02	0.02	-1.95	-0.02
HPO_4^{2-}	-0.02	-0.04	**n. d.**	0.02	**n. d.**	-0.01	0.00	**n. d.**	**n. d.**	0.00	0.00	0.03	**n. d.**

quotient (~ RQ). Variations in the RQ value were observed between stations as well as over time at a given station. The RQ term can provide general information regarding the pathways responsible for organic carbon oxidation. For example, an RQ of 1 would suggest that aerobic processes dominate carbon oxidation because during aerobic oxidation, one mole of O_2 consumed for each mole of CO_2 produced, thus producing a RQ = 1 if only aerobic oxidation is important.

An RQ > 1 suggests that anaerobic and suboxic processes contribute to net carbon oxidation. Furthermore, for the RQ to average > 1, net burial of reduced end products must occur (see below). For example, for every mole of sulfate reduced, two moles of DIC are produced. Other anaerobic (e.g. denitrification) and suboxic (e.g. iron or manganese reduction) reactions vary in the amount of DIC (moles) produced per mole of electron acceptor oxidized. Generally speaking, however, if the RQ is > 1, other processes, usually assumed to be primarily sulfate reduction, in addition aerobic respiration, must be occurring. For the RQ to be maintained at > 1, the produced sulfide must not be re-oxidized, as sulfide oxidation would consume O_2 and push the RQ back towards 1. The average RQ among all stations was approximately 2, suggesting that suboxic and anaerobic processes contribute significantly to benthic metabolism and that reduced end products, such as sulfide in the form of pyrite (FeS_2), accumulate (over at least annual time scales) in the sediments.

The possibility that benthic production is important in this system complicates the interpretation of our benthic flux data. Benthic production probably leads to diel patterns of DIC and SOD. This means that nutrient cycles are potentially radically altered, such that sediments could serve as sinks for nutrients during the day via uptake by benthic phototrophs but as sources for nutrients at night when phototrophs are not active. Active benthic photosynthesis would also lead to dramatic diel shifts in redox barriers. The presence of mobile redox fronts has particularly important implications for the P cycle.

Diel experiments conducted at the Texas City and East bay sites suggest that there is indeed a phototrophically-driven diel pattern in denitrification, SOD, DIC fluxes and nutrient fluxes. These data are currently being modeled by S. An and a separate paper is being prepared on this subject. In our 1996 report (Joye and An 1997), we discussed our first diel experiment, which was conducted in Texas City. We found that the SOD decreased during the day while the denitrification rate increased. We hypothesized that resulted from the stimulation of coupled nitrification-denitrification in the presence of benthic photosynthesis. This also suggests rapid biogeochemical cycling in the upper few cm of sediment with production and consumption of benthic microalgal derived organic matter being tightly coupled in space and time with nutrient mineralization processes. Similar results have been obtained during 1997.

Obvious evidence for benthic primary production is seen the evolution of O_2 in Station 3 benthic chambers during August and November of 1997 and during January 1998. Denitrification exhibits a dramatic diel pattern that is apparently coupled to, and possibly driven by, benthic photosynthesis; this is the first time that this kind of data has been collected in an estuarine ecosystem.

Controls on denitrification. In order to evaluate the environmental controls on denitrification in Galveston Bay, we pooled all of our data and correlated selected parameters with either nitrate concentration and/or the denitrification rate. ANOVA are currently being performed on selected portions of our data set. Temperature and salinity were poor predictors of nitrate concentration (Fig. 26). There is no clear relationship between nitrate concentration and salinity. Low salinity waters generally have higher nitrate concentration than do high salinity waters; increases in concentration were sometimes observed at intermediate salinities (4 and 15 ppt), possibly due to nitrification. Lower temperature waters had higher nitrate concentrations. The denitrification rate was not correlated with salinity (Fig. 27), nor was the rate well-correlated with bottom water nitrate concentration (Fig. 28). There was a relationship between temperature and the denitrification rate, with rates increasing by 2-5 times over a 15 °C temperature range (Fig. 28). Neither the DIC nor the DIN flux was a good predictor for the denitrification rate (Fig. 29). If the data are separated by site, some of the scatter is reduced (Fig. 30); however, the regressions do not yield r^2 values above 0.6.

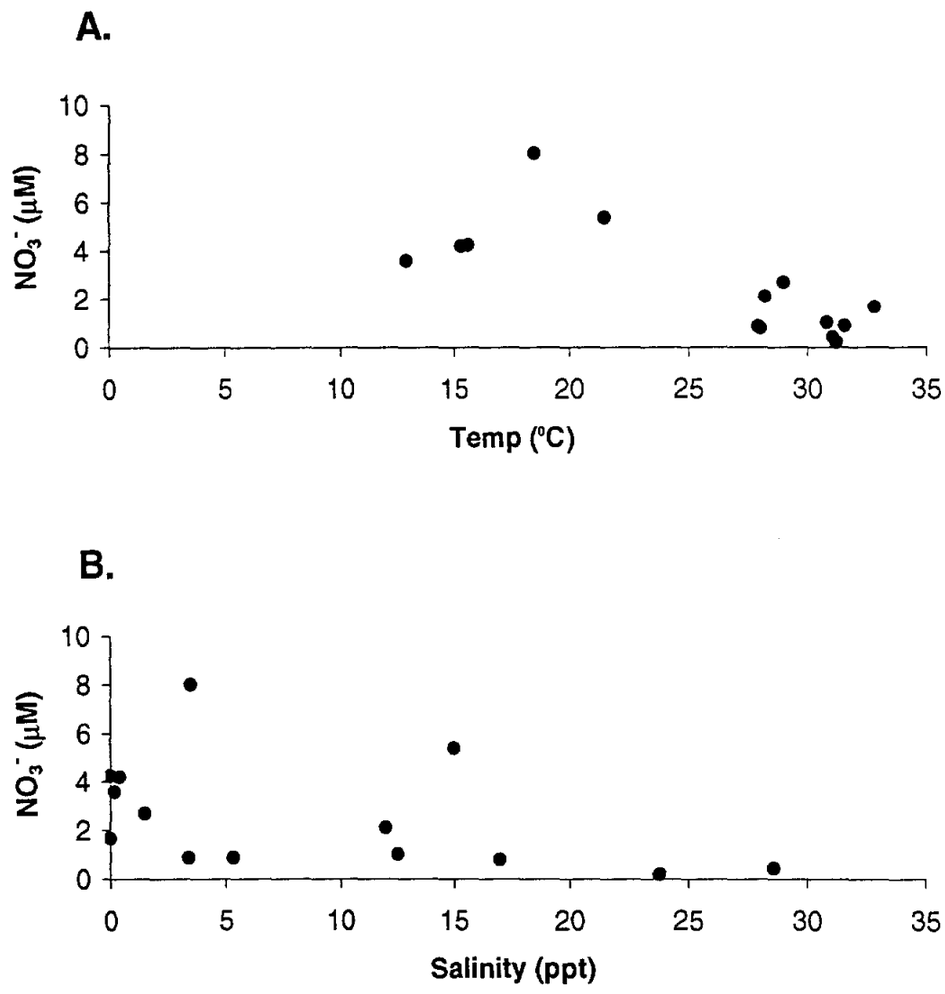

Figure 26. Relationship of bottom water NO_3^- concentration in Galveston Bay with temperature (A) and salinity (B).

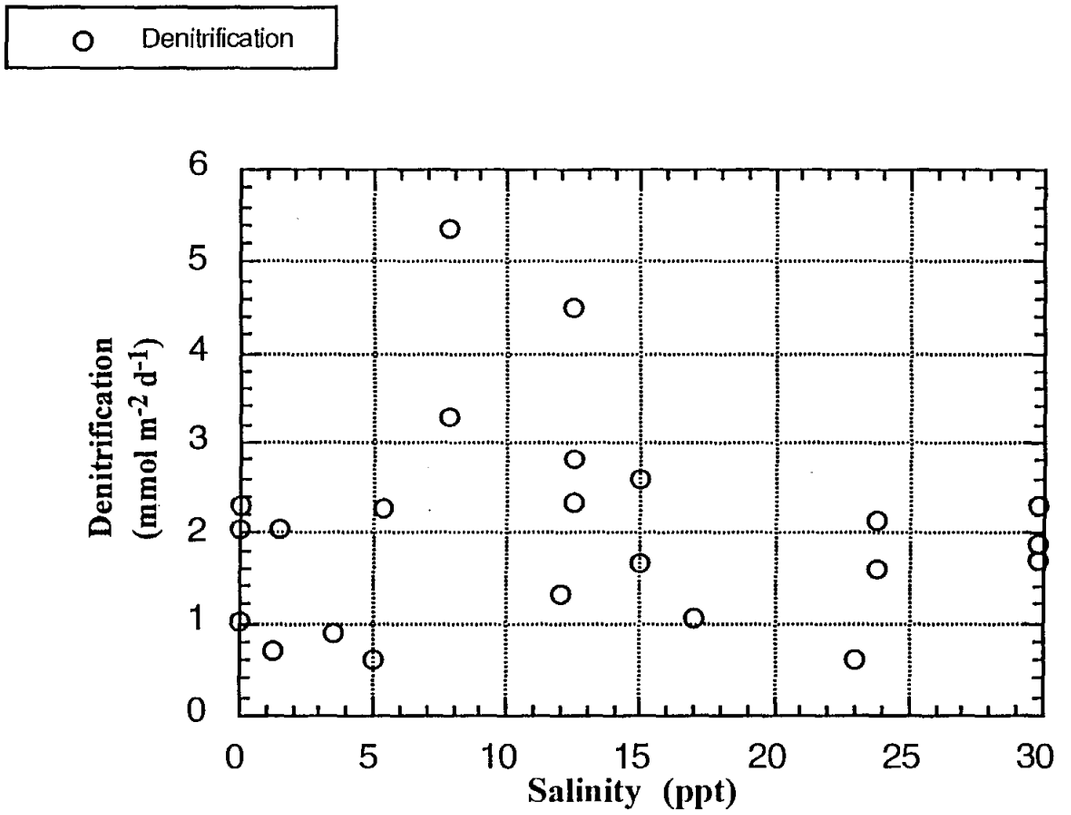

Fig. 27. Denitrification plotted against salinity. Data are pooled from all stations and seasons.

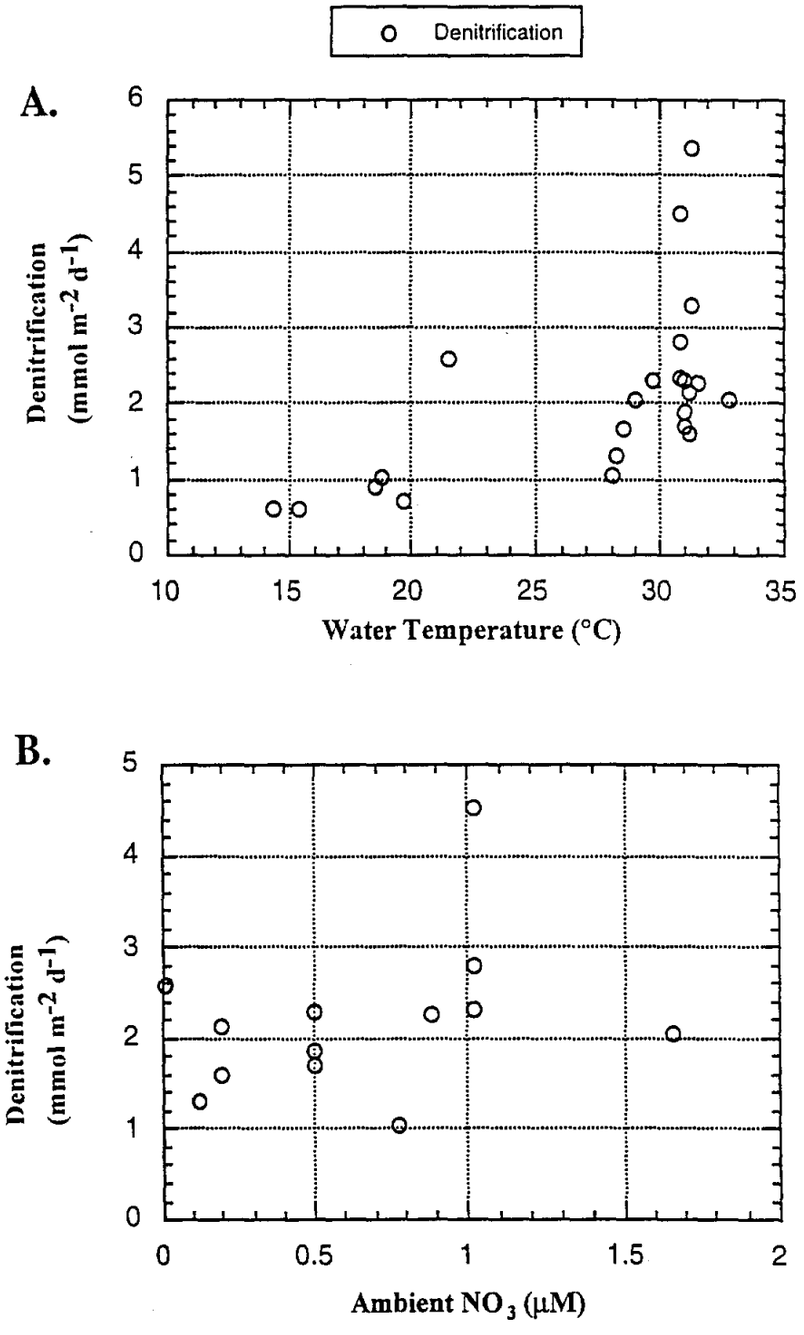

Fig. 28. Denitrification plotted against temperature (A) and ambient NO_3 concentration (B). Data are pooled from all stations and seasons.

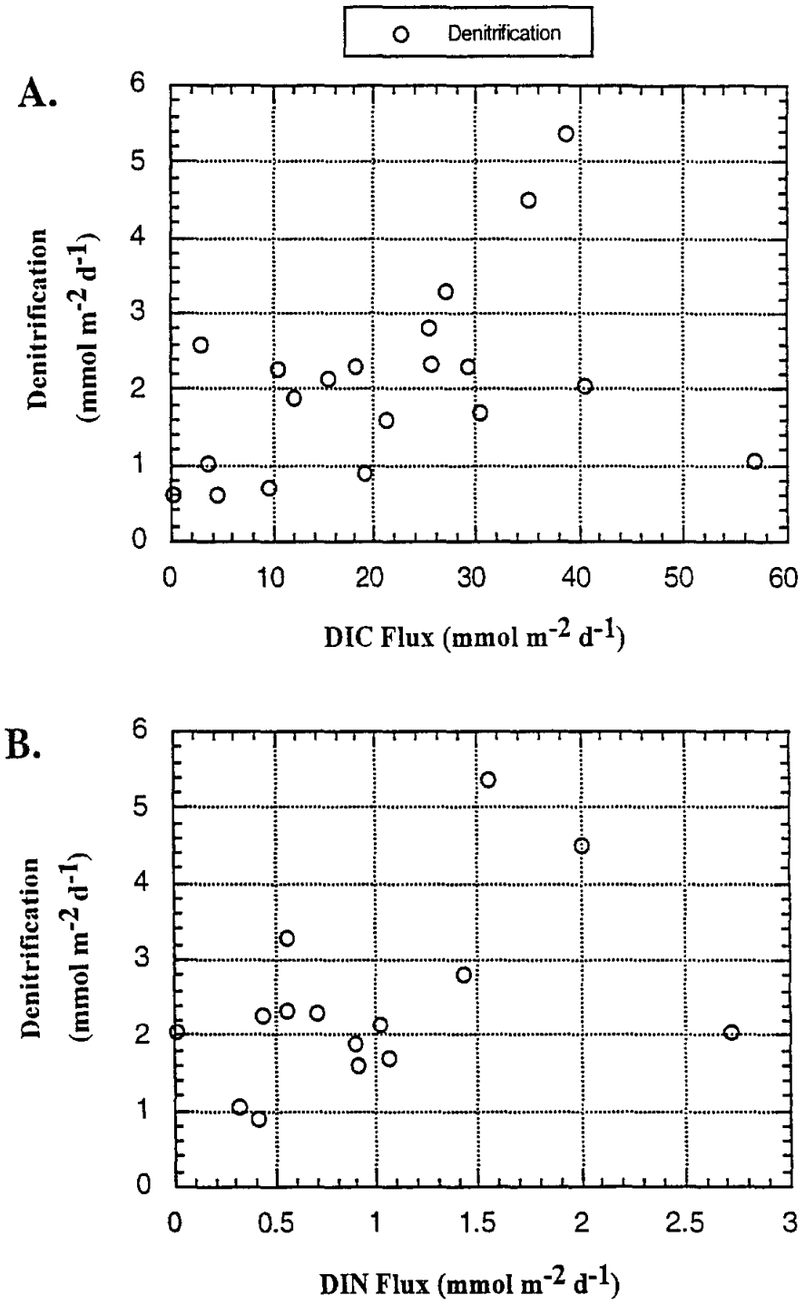

Figure 29. Denitrification rate plotted against the DIC flux (A) and the DIN flux (B). All rates in mmol m^{-2} d^{-1}.

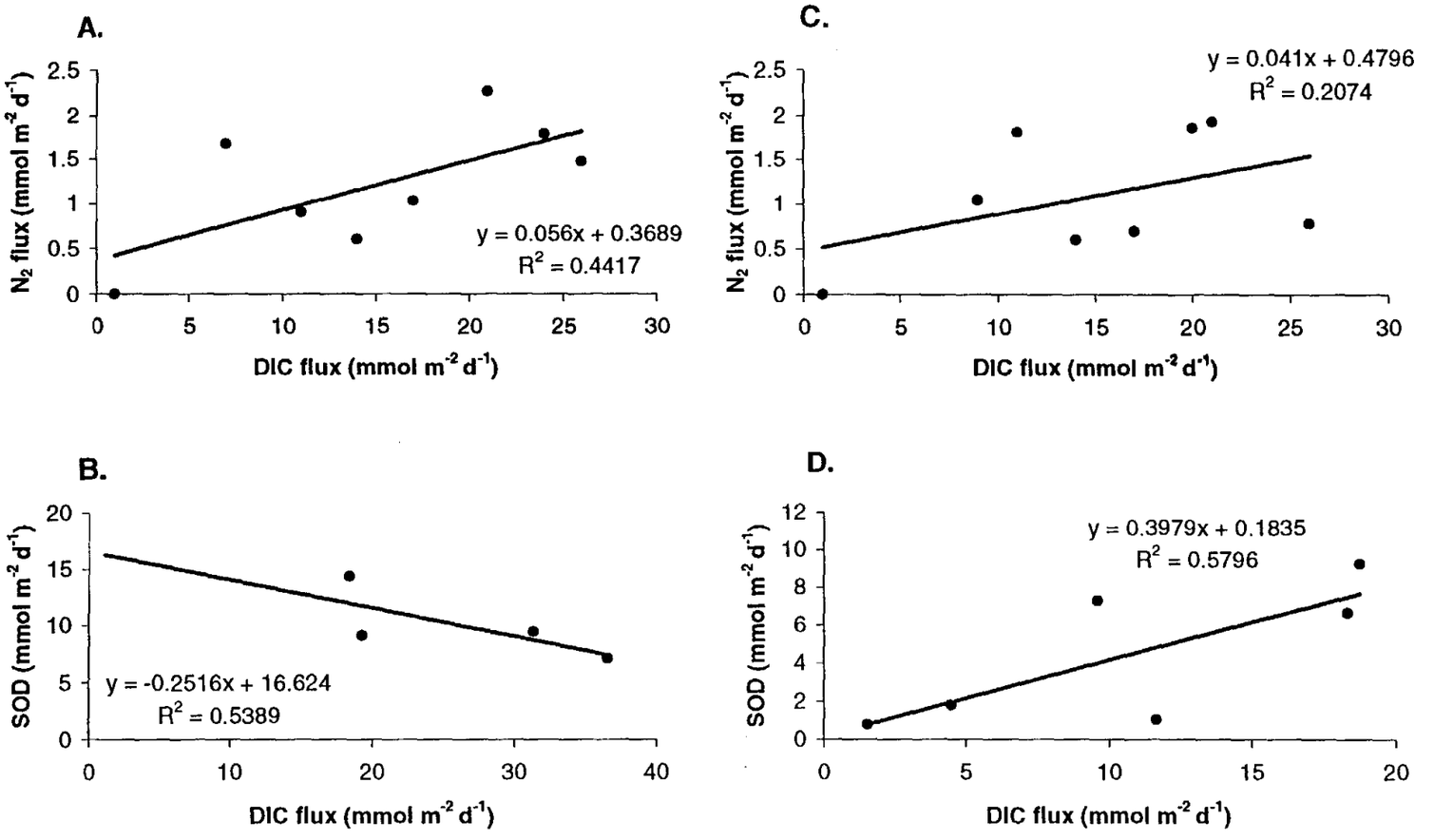

Figure 30. Relationship between denitrification and the DIC flux for Station 4 (A) and Texas City (C) and between the sediment oxygen demand and DIC flux for Station 4 (B) and Texas City (D).

In order to improve the regressions, we separated our data based on sediment type (coarse sands or fine muds). Sediment type can be roughly correlated with organic carbon content. In Fig. 31, we present temperature vs. denitrification correlations for coarse and fine sediment types. The regression for the coarse grained sediments is quite good and the distribution of points spans a the range of temperatures that occur seasonally in Galveston Bay. A reasonable function is also obtained for fine-grained sediments, however, the data are skewed on the high temperature end. However, this approach provide the best means to obtain functions for predicting denitrification based on temperature. A similar approach was used by Brock et al. (1996) to hind-cast denitrification rates in Galveston Bay.

Modeling denitrification rates. For the purpose of estimating bay-wide denitrification rates and assessing N removal rates, we used the equations presented in Fig. 30 and the annual average temperature data obtained from the TNRCC data base to calculate annual bay-wide denitrification rates. We then assessed the bay-wide distribution of sandy vs. muddy sediments using USGS maps of sediment distribution. Weighting functions were applied based on the km^2 coverage of coarse- and fine-grained throughout the Bay. By knowing the percent of Bay floor covered by each sediment type, we applied the appropriate regression and estimated denitrification rates.

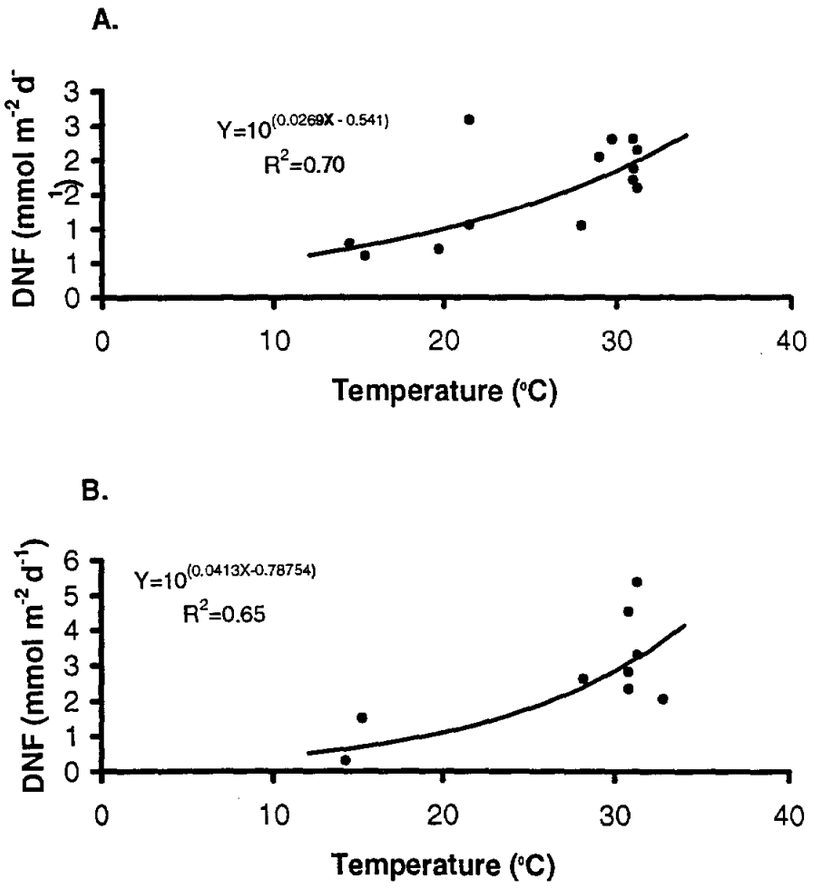

Figure 31. Relationship between temperature and denitrification rate in coarse (% sand > 80, A) and fine grained (B) sediment in Galveston Bay.

This approach provided whole Bay denitrification estimates over an average annual temperature cycle (Fig. 32). Next, the N loading rate to the Bay was obtained from the TNRCC data base and from Brock et al. (1996). In Fig. 32, we show the monthly integrated N loading rate, whole-bay denitrification rate, and % of N load lost via denitrification over a generic annual cycle.

While N loading is maximal during the spring, denitrification rates are maximal during late summer and fall. This results in low % N removal during spring but in efficient N removal during summer. The average N removal rate is approximately 55% of the N load (solid line). If we take a different approach and average all of our benthic flux data and extrapolate that average over the entire area of the Bay, we obtain a similar number (50%). The fact that these numbers are similar suggests that the denitrification-temperature relationship provides a reasonable method by which to hindcast or forecast N removal over annual cycles with varying temperature and/or N-loadingscenarios.

Our 55% N removal estimate is much greater than the 7% value estimated in Zimmerman and Benner (1994) and are lower than the 66% removal estimated by Rowe et al. (submitted). Our estimates are probably better than either the Zimmerman and Benner or the Rowe et al. estimates because the measurements were made *in situ* (Zimmerman and Benner's were not) and the measurements were made over two annual cycles (Rowe et al's data represent only summer values). Applying

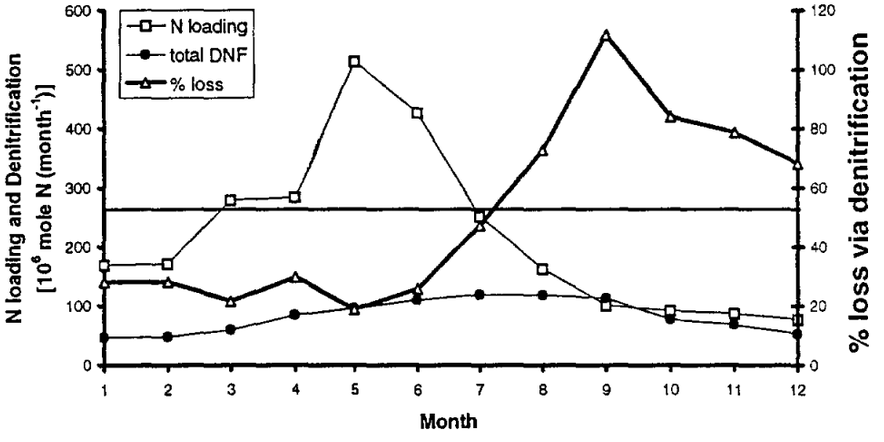

Figure 32. Whole system denitrification, nitrogen loading and % N load loss via denitrification in Galveston bay. The rate was calculated using our denitrification rates in the relationship: DNF = a x 10(b x temp) (see text). The horizontal line represents the average % removal.

indirectly obtained or seasonally-limited data to the entire ecosystem with the hope of obtaining accurate estimates of bay-average activity can sometimes yield spurious results. In particular, the results of Zimmerman and Benner were probably serious underestimates because their method unintentionally de-coupled denitrification and benthic photosynthesis. Our diel data clearly illustrate the importance of coupling between these processes and de-coupling them would almost certainly result in severe underestimates of denitrification rates.

While our data set is by no means perfect (for example, our current fine-sediment denitrification - temperature relationship needs refinement and improvement and we need to work more at stations in the Central Bay), we believe it does represent a significant improvement in the data available. One high removal estimate (55%) is approximately 20% higher than that which would be predicted based on the hydraulic residence time - denitrification relationship (i.e., ~ 35%) presented by Nixon et al. (1996) and Nowicki et al. (1997). The fact that denitrification and benthic photosynthesis are closely coupled may serve to enhance the removal efficiency of nitrogen in this system and cause Galveston Bay to act differently from the other systems considered in the model.

To assess how good our direct estimates of denitrification were, we compared the stoichiometrically estimated denitrification rates to that were determine directly (Joye et al. 1997). Generally speaking and within the error of the measurements, our

direct *in situ* estimates are quite good (see Figs. 33 & 34). Estimates of total N regeneration were obtained by applying DIN:DIC stoichiometry to the benthic DIC flux data (Joye et al. 1996). This allowed us to predict how much DIN should have fluxed from the sediment. Then, we compared the measured fluxes of N_2 and DIN to the predicted amount of DIN production.

At the Texas City station, the sum of dissolved N_2 and DIN fluxes almost equals the regenerated DIN flux predicted from DIN:DIC stoichiometry. If we partition the regenerated N flux between DIN and N_2, we see that between 50-100% of N regeneration flows through denitrification at this site. In contrast, at Station 4, on three of four occasions, the dissolved N_2 and DIN fluxes were below that predicted based on DIN:DIC flux stoichiometry. At this station, there was a fairly consistent 50:50 split between regeneration and denitrification. So, while our data do a good job of balancing the benthic N budget at Texas City, we are missing about 30-50% of the regenerated N at Station 4. This N may be fluxing from the sediments as urea, other DON, or as N_2O; we are not measuring any of those pools as part of this study at this time. However, some N_2O measurements are planned during 1998.

Potential Denitrification. In order to evaluate the effect of temperature and nitrate, organic carbon and sulfide concentration on denitrification, laboratory experiments were conducted using sediment collected from Station 4 in November 1997. As expected, denitrification rates increased with increasing nitrate concentration when

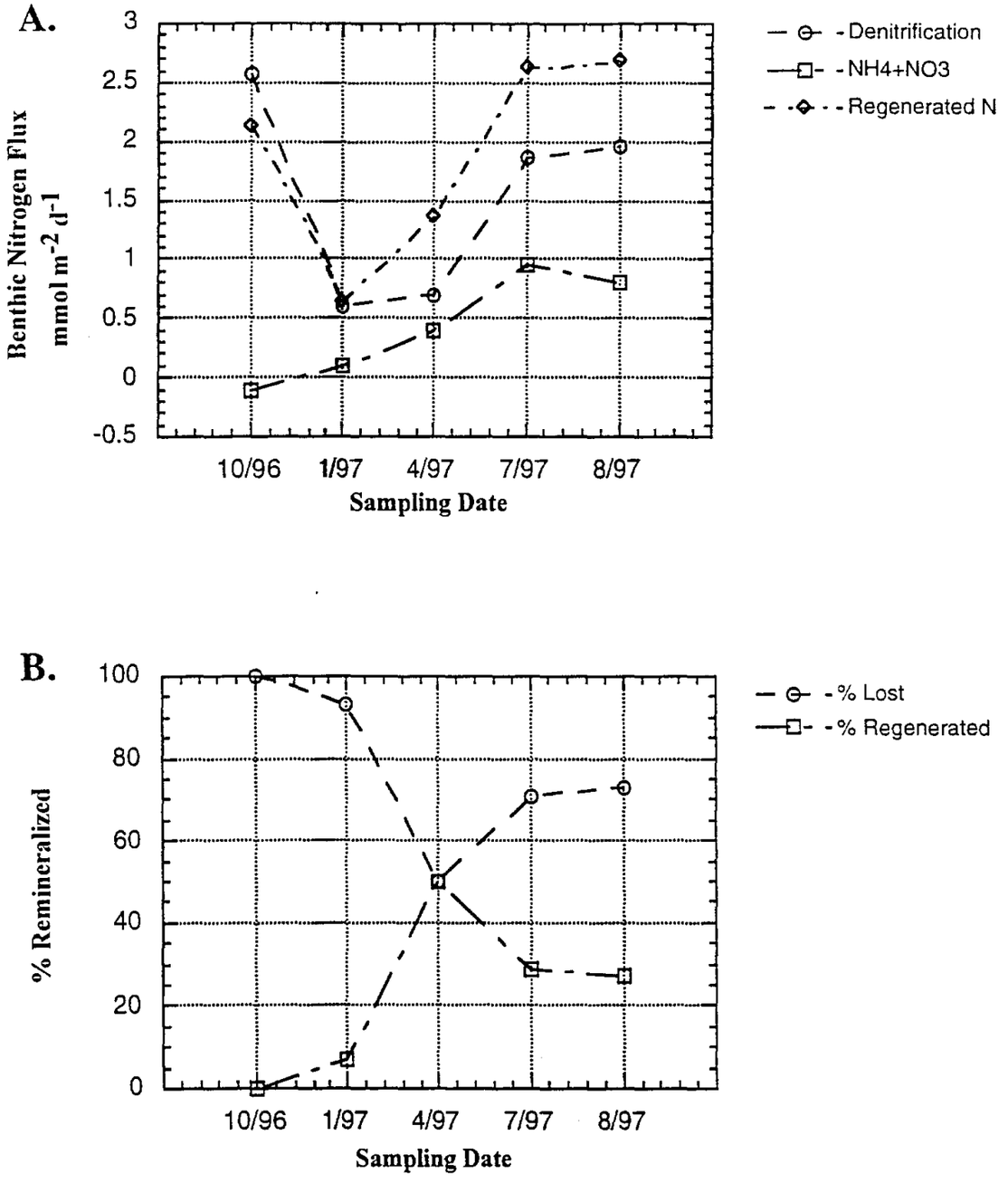

Fig. 33. A. Denitrification (o), DIN flux (□), and N regeneration (◇) in Texas City sediments. B) The % of the benthic N flux lost via denitrification (o) versus reveneration (□) as DIN.

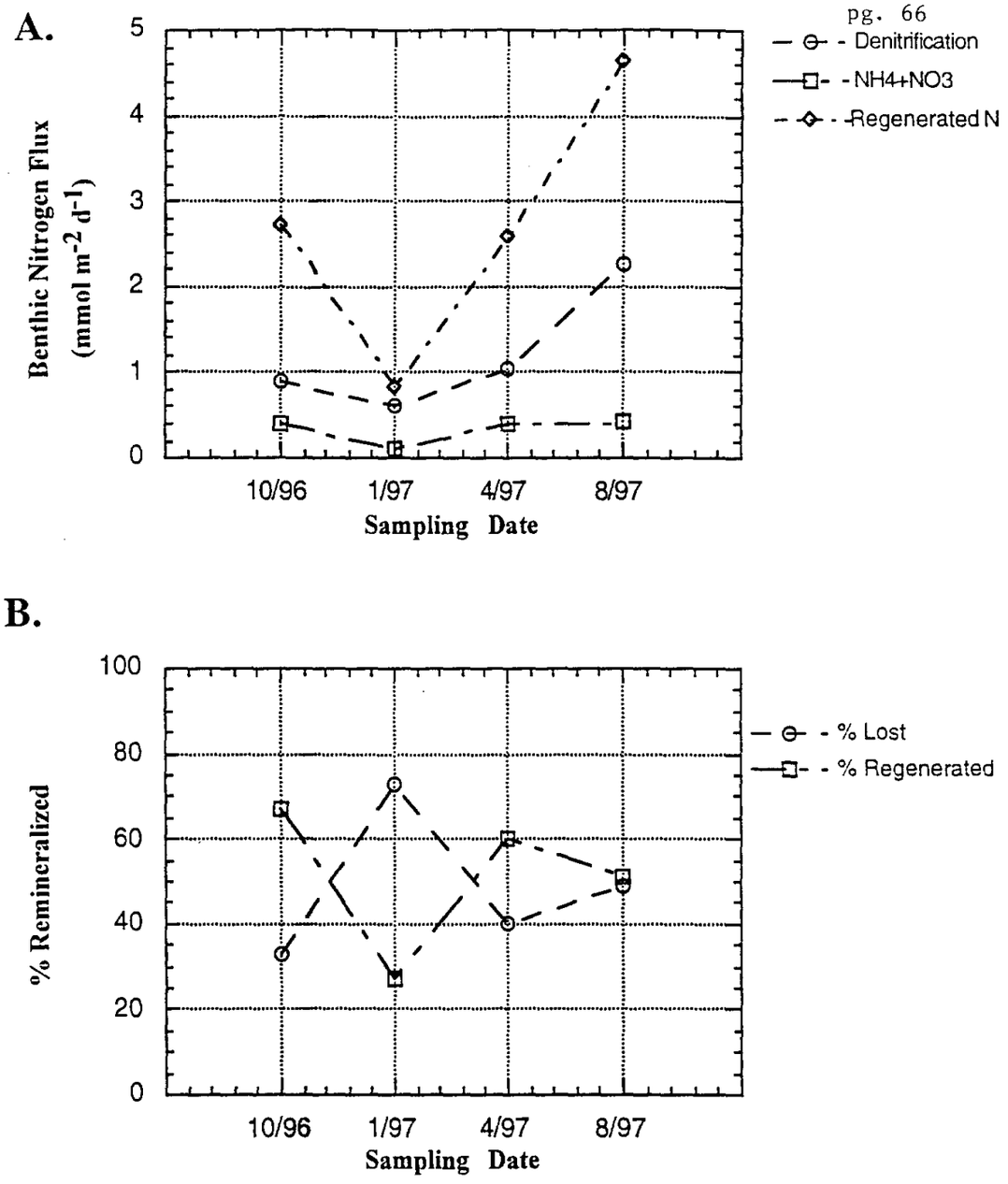

Fig. 34. A. Denitrification (o), DIN flux (□), and N regeneration (◇) in Station 4 sediments. B. The percent of the benthic N flux lost via denitrification (o) versus reveneration (□) as DIN.

sediment slurries were incubated at 23 °C (Fig. 35). Rates were approximately 3 times higher when samples were incubated at 23 compared to 4 °C; in fact, no clear concentration effect was observed in the 4 °C samples. The addition of glucose did little to stimulate denitrification rates as there was no significant difference between treatments receiving no glucose and those amended with 1000 μM glucose. Similarly, we observed no negative effect of sulfide addition on N_2 evolution. These results suggest that denitrification is limited primarily by temperature, and secondarily, by nitrate availability, which corroborates the results of our field studies.

IV. Conclusion s and 1998 work

The results obtained during our study thus far (1996-1997) suggest the need for a re-evaluation of the N budget of Galveston Bay. Our estimates of bay-wide average denitrification rates and annual N removal suggest high N removal rates, between 50-55%. This bay-wide model will be fine tuned during 1998 by sampling an additional station in the Central Bay region, North of Texas City, and by obtaining more data in the lower temperature range (during Jan 1998) for the fine sediment types. We will continue to monitor activity in the East Bay site (in April) and Station 5 in the Trinity (in April and October). Diel studies will continue at the Texas City and East Bay sites so that we can evaluate the importance of benthic production as well as investigate the link between benthic production and denitrification. We will continue to monitor benthic chlorophyll distribution as well. When our program is

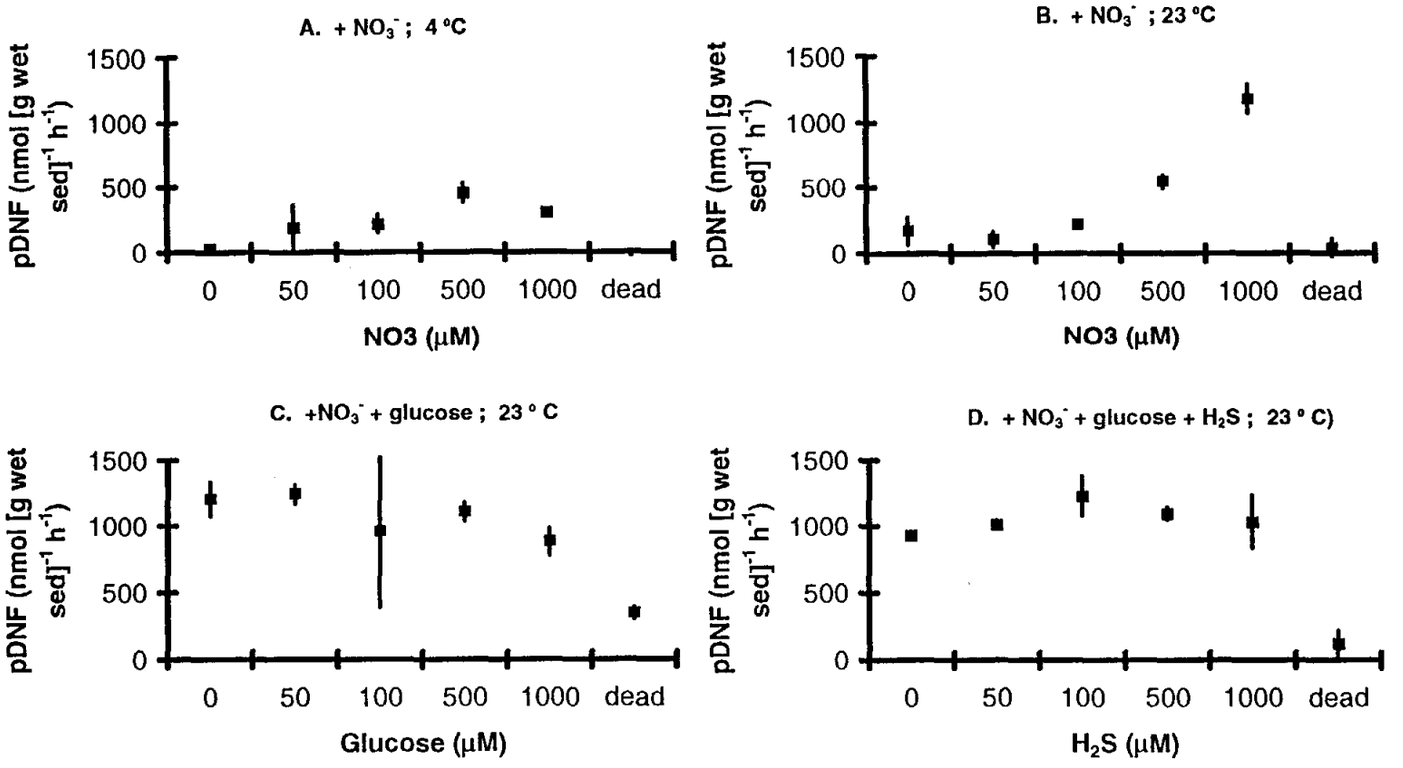

Figure 35. Nitrogen gas production (nmol N_2 [g wet sediment]$^{-1}$ h^{-1}) in NO_3^- amended (all panels), temperature varied (A & B), glucose amended (C), and sulfide amended (D) samples.
Points represent the average rate in three replicates; bars denote the standard deviation of the mean.

completed, we undoubtedly have a much clearer understanding of the benthic N cycle in Galveston Bay.

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Table 4A. Station 1 porewater nutrient concentrations (µM)
Empty cells denote no data.

depth	NH_4^+						NO_3^-					
(cm)	Jun-96	Jul-96	Aug-96	Apr-97	Jul-97	Nov-97	Jul-96	Aug-96	Jan-97	Apr-97	Jul-97	Nov-97
0-1	162.3	11.8	11.8	26.3	50.5	91.3	6.6	8.2	9.4	33.3	24.8	4.0
1-2	45.0	13.1	13.1		38.4	149.0					25.7	9.6
2-3				23.7	25.8	106.1		9.9	7.5	20.0	48.6	6.9
3-4					287.8	124.6					62.6	5.2
4-5					42.4	134.9		3.3	7.9	17.4	15.9	6.6
5-8	167.4	28.4	28.4		15.7	232.6	0.8	2.5	6.5	19.4	18.8	5.5
8-11	148.3	74.3	74.3	70.7	19.7	302.9		6.6	6.3	10.2	12.5	4.4
11-15	172.5	43.7	43.7	167.1	20.2	356.2		4.8	26.8		30.9	1.4
15-20	30.9			338.3	36.4	406.5		10.7			10.2	3.3
20-25	414.8	11.8	11.8		31.3						13.3	
25-30					16.7						27.2	
30-35					34.3						15.8	

	HPO_4^{2-}						
(cm)	Jun-96	Jul-96	Aug-96	Jan-97	Apr-97	Jul-97	Nov-97
0-1	4.4	3.5	1.8	3.3	2.1	4.9	0.3
1-2	0.9					0.0	6.7
2-3			8.0	6.7	4.2	1.1	0.3
3-4						0.0	0.2
4-5			18.6			0.0	0.0
5-8	1.8	1.8	5.3			0.0	0.7
8-11	0.9	1.8	11.5	2.4	1.5	0.4	0.0
11-15	2.7	3.5	11.5	2.2	1.4	0.0	0.0
15-20			8.9	0.5	0.3	0.0	0.0
20-25						0.8	
25-30						0.0	
30-35						0.1	

Table 4B. Station 2 porewater nutrient concentrations. Empty cells denote no data.

	NH_4^+			NO_3^-	HPO_4^{2-}	
(cm)	Jun-96	Apr-97	Jul-97	Jul-97	Jun-96	Jul-97
0-1	81.9	53.0	105.9	1.9	3.5	0.0
1-2	171.2		64.1	19.6	2.7	0.2
2-3	184.0	14.1	117.2	23.5	2.7	1.0
3-4	423.8			23.6	10.6	1.4
4-5		23.2	49.5	8.0		1.4
5-8	464.6		43.4	4.7	17.7	0.7
8-11	277.1	90.4	78.3	10.9	11.5	1.0
11-15		14.6	53.0	2.0		0.0
15-20		8.6	564.5	0.0		1.3
20-25		29.1	640.3	0.0		0.3
25-30			550.9			

Table 4C. Station 3 porewater nutrient concentrations.
Empty cells denote no data.

depth	NH_4^+							NO_3^-		
(cm)	Jun-96	Jul-96	Aug-96	Oct-96	Apr-97	Jul-97	Nov-97	Aug-96	Oct-96	Apr-97
0-1	301.3	295.0	150.8	314.5	285.8	1170.0	86.1	1.6	12.3	7.8
1-2	663.6	442.3	196.7	380.2	299.9	115.6	89.8	3.3	10.0	34.9
2-3	627.9	524.5		479.1	390.3	134.8	140.8		18.0	1.0
3-4		464.6		38.1	291.4	132.8	180.8		12.3	26.5
4-5	934.0	317.9		705.2		36.4	373.2		2.5	
5-8	627.9	662.3	413.6	1132.8	820.1	412.1	712.2	6.8	13.3	
8-11	583.2	833.2		977.3	816.5	1225.5	960.1		25.9	19.2
11-15	962.0	960.8	823.0	1754.7	991.7	187.8	1239.9	4.1	26.8	14.5
15-20	1270.7	890.6		2104.5		135.3	1236.2		11.9	
20-25	1218.4	842.1	986.3	2088.9		73.2	1296.8	8.2	14.7	
25-30		321.7	1310.2	2120.0		87.4	1558.8	6.0	13.8	
30-35		249.0		1754.7				19.7	11.4	
35-40		229.9	1166.1	1521.5				23.8	10.5	

depth	NO_3^-		HPO_4^{2-}						
(cm)	Jul-97	Nov-97	Jun-96	Jul-96	Aug-96	Oct-96	Apr-97	Jul-97	Nov-97
0-1	34.0	8.0	1.8	4.4	1.8	5.8	4.3		
1-2	3.6	6.6	0.9	13.3	1.8	5.0	4.6	0.5	0.9
2-3	23.0	6.3	0.9	31.0		6.2	-0.2		0.4
3-4	16.9	21.5	1.8	11.5		2.1	24.3		2.4
4-5	8.1	7.9	1.8	22.2		0.8			
5-8	7.9	3.1		40.8	0.9	6.2	4.3	1.2	
8-11	8.4	4.3	4.4	76.3			7.3	13.2	1.1
11-15	7.0	2.5	0.9	33.7		22.8		7.3	
15-20	12.4	5.2	0.9	5.3		0.8		5.7	0.8
20-25	8.5	4.2	0.9	7.1	0.9	5.4		0.3	1.0
25-30	11.3	3.2		32.8	2.7			0.6	
30-35				32.8					
35-40				1.8	4.4	12.0			

Table 4D. Station 4 porewater nutrient concentrations.
Empty cells denote no data.

depth	NH_4^+							NO_3^-			
(cm)	Jun-96	Jul-96	Aug-96	Oct-96	Apr-97	Jul-97	Nov-97	Jul-96	Aug-96	Oct-96	Jan-97
0-1	269.4	499.0	124.0		168.7	987.2	199.3	25.5	2.0		4.2
1-2		598.5	191.6		143.4	105.0	211.1	4.1	6.6		7.0
2-3	342.1	770.7	218.4	151.2	108.1	163.1	317.7	0.0		20.8	3.9
3-4	217.1	986.3	333.2		299.0	471.1	351.0	9.2	9.2		4.0
4-5	292.4	1189.1	358.7	215.5	58.6	314.1	344.4		6.4	5.8	7.3
5-8	478.6	1298.8	352.3	81.2		338.8	778.8		12.3	17.0	5.9
8-11	678.9	1810.2	455.7	133.5		775.6	1190.3	8.0	3.6		3.8
11-15	1096.0	1765.6	455.7	43.8	268.1	774.1	1410.1	12.8	3.3	10.9	3.2
15-20						849.8	1091.8				
20-25			761.8	89.7	97.0	951.9	1573.6	5.2	4.4	15.6	
25-30			666.1	104.6		1018.0	1464.8			15.2	
30-35			858.7	45.2					8.8		
35-40			458.2	69.9					10.7		

depth	NO_3^-			HPO_4^{2-}							
(cm)	Apr-97	Jul-97	Nov-97	Jun-96	Jul-96	Aug-96	Oct-96	Jan-97	Apr-97	Jul-97	Nov-97
0-1	2.2	15.0	7.7	8.9		2.7		2.6	10.3	4.5	0.2
1-2	14.0	58.8	17.7		7.1	6.2		0.8	77.4	6.0	0.4
2-3	15.9	11.5	15.3	5.3	1.8	2.7	103.7	-0.1	59.8	7.7	0.9
3-4		11.2	13.3	2.7		1.8		0.0		9.7	1.4
4-5		9.2	13.2	8.0		2.7	248.1	1.4		14.6	1.4
5-8	16.0	6.3	7.5	5.3	17.7	1.8	48.9	1.0	33.4	2.4	1.5
8-11		9.8	8.6	44.3	1.8	0.9	16.6	0.2		19.7	0.0
11-15		12.0	9.1	4.4	1.8	1.8		0.1		34.3	0.0
15-20		21.2	8.5					0.1		12.6	0.2
20-25		21.6	8.5	1.8	2.7	2.7	9.5			10.8	0.0
25-30		21.6	9.8				24.1			3.2	0.1
30-35						2.7					
35-40						0.9					

Table 4E. Station 5 pore water nutrient concentration. Empty cell = no data.

depth (cm)	NH_4^+	NO_3^-	HPO_4^{2-}
0-1	345.4	8.2	0.1
1-2	520.6	7.3	
2-3		7.6	0.2
3-4	734.7	8.0	0.0
4-5	685.2	4.6	0.1
5-8	847.3	4.4	0.2
8-11	818.5	4.2	0.2
11-15	769.6	3.5	1.2
15-20	699.9	7.9	1.0
20-25	902.9	15.8	0.0
25-30	1148.8	5.4	0.2

Table 4F. East Bay pore water nutrient concentration. Empty cell = no data.

depth (cm)	NH_4^+	NO_3^-	HPO_4^{2-}
0-1	152.5	8.2	0.2
1-2	297.5	7.3	0.1
2-3	796.8	7.5	0.1
3-4	366.1	8.0	0.9
4-5	591.3	4.6	0.0
5-8	345.9	4.4	
8-11	231.3	4.2	0.8
11-15	196.9	3.5	0.2
15-20	200.0	7.9	0.2