

# Denitrification in Galveston Bay Final Report

A final project report submitted to the  
Texas Water Development Board

by:

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### **Preface and Acknowledgements**

The following report presents an overview of three years of research on denitrification in Galveston Bay, Texas. Portions of this report have been adapted from the Ph. D. dissertation of Soonmo An (Texas A&M University, May 1999). This work was supported by contracts to S. B. Joye from the Texas Water Development Board (TWDB 96-167, TWDB 97-218, and TWDB 98-239) and grants to S. B. Joye from the National Science Foundation (OCE 96-96054 and OCE 98-96216). We thank L. Alford, S. Carini, R. Downer, S. Escorcia, J. Hohman, R. Lee, K. Mace, A. Pichachy, S. Ravula and S. Miller for assistance in the field and in the laboratory related to this project. SBJ would like to thank D. Brock, P. Eldridge, J. Pinckney and L. Cifuentes for stimulating and insightful discussions about the Galveston Bay ecosystem.

## I. Introduction

Coastal environments support extensive biodiversity and provide habitats for valuable commercial fish stock. They house large reserves of mineral resources (petroleum, natural gas, phosphates) and support recreational industries that often form the financial backbone of smaller coastal communities. These ecosystems are inherently complex: their physical, biological and chemical dynamics are tightly coupled and are characterized by a multitude of feedback mechanisms that operate on a variety of spatial and temporal scales. For the appropriate management and restoration of estuaries, a comprehensive understanding of source and sink terms of nutrients and materials is essential (Wollast 1983; McClelland and Valiela 1997). The fundamental understanding of these ecosystems therefore requires a process-oriented, integrated and comparative approach. We have used this approach to examine N cycling in Galveston Bay, Texas.

Nitrogen availability frequently limits primary production in marine environments, including estuaries (Ryther and Dunstan 1971; Capone and Kiene 1988). Denitrification affects N availability for primary production by transforming combined N to forms less available to biota ( $N_2$  or  $N_2O$ ; Seitzinger 1988; 1990). The source of the  $NO_3^-$  used for denitrification comes from water column influx or *in situ* nitrification (Sørensen et al. 1979; Nishio et al. 1982; Jenkins and Kemp 1984). In many estuarine environments, 70-100% of  $NO_3^-$  consumed by denitrifiers is derived from *in situ* nitrification (Sørensen et al. 1979; Jenkins and Kemp 1984). This is commonly referred to as 'coupled' nitrification-denitrification. Quantifying *in situ* rates of N transformations, including N regeneration, nitrification and denitrification, and identifying linkages between these processes is essential for developing a system-level N budget for Galveston

Bay. Detailed N budgets provide a basis from which to predict the overall system response to perturbation, including those resulting from cultural eutrophication.

The cycling of nitrogen (N) between the compartments of a given ecosystem is driven primarily by microbially-mediated processes, including N uptake, dinitrogen (N<sub>2</sub>) 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 N loss from an ecosystem (via denitrification). Dinitrogen gas can serve as a nutritional N source to only a limited suite of microorganisms (N<sub>2</sub> fixers; Knowles 1982; Howarth et al. 1988; Zumft et al. 1988). The process of denitrification thereby serves to remove combined N from the biologically available pool as denitrifying microorganisms transform nitrate or nitrite to gaseous forms, N<sub>2</sub> or nitrous oxide (N<sub>2</sub>O). Denitrifying bacteria respire nitrate when oxygen (O<sub>2</sub>) concentrations are below 20 μM; Knowles 1982; Tiedje et al. 1989); however, some O<sub>2</sub> 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 NO<sub>3</sub> concentration but temperature and the concentration of organic carbon, O<sub>2</sub> and hydrogen sulfide (HS<sup>-</sup>) also influence activity (Koike and Sørensen 1988; Seitzinger 1988, 1990; 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 NO<sub>3</sub>

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  $NO_3$  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 regeneration occurs (Joye et al. 1999). After internal regeneration processes, some portion is returned to the water column as dissolved inorganic N [DIN =  $NO_2 + NO_3 + NH_4$ ]: 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” fraction. Finally, some portion of regenerated  $NH_4$  may be permanently buried in sediment porewater. The buried fraction represents a long term sink for N in the system. However, in the context of nutrient regeneration and the sustenance of system production on the short term, the difference between the regenerated and denitrified fractions is the most important consideration (Joye et al. 1999).

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<sup>-2</sup> d<sup>-1</sup> (Seitzinger 1988), while nitrification rates range between 0 - 5 mmol N m<sup>-2</sup> d<sup>-1</sup> (Henriksen and Kemp 1988). Spatio-temporal variations in temperature, organic carbon supply, and O<sub>2</sub> and HS<sup>-</sup> 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 estuarine ecosystem is the second largest estuarine complex along the Texas coast. Galveston Bay 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 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 higher nutrient



loadings that are delivered more uniformly compared to historical trends of pulsed events of rainfall runoff and freshwater inflows.

Planning for the future of the Galveston Bay ecosystem requires integrating the needs of the surrounding watershed (both metropolitan and industrial uses) with the needs of the estuary. Changes in freshwater inflow result in decreased particulate and dissolved nutrient inputs, modifications of salinity structure, alterations of residence time, et cetera. Feedback and interaction between these three parameters (nutrient inputs, salinity structure and residence time) can, in turn, serve to regulate/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, preliminary results have shown that nutrient loading may be as important a consideration as inflows needed to maintain salinity gradients or other factors. Assessment of nutrient requirements depends on adequate knowledge of the nutrient budgets of the estuarine system, and work has been done to compile meaningful budgets for Galveston Bay (Brock et al. 1996). However, the budget exercise revealed areas, such as knowledge of denitrification, where rates of important processes were not well known. Without good knowledge of the way 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. 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.

Previous estimates of denitrification in Galveston Bay sediments have provided two strikingly different scenarios. The average denitrification rate was found to be  $480 \mu\text{mol N m}^{-2} \text{ d}^{-1}$  by Zimmerman and Benner (1994). Modeling of these data suggests that denitrification removes 7% of the N on a bay-wide basis (Brock et al. 1996). In contrast, Rowe et al. (submitted) estimated a bay-wide average denitrification rate of  $10 \text{ mmol N m}^{-2} \text{ d}^{-1}$  from benthic flux O:N stoichiometry. This estimate of denitrification suggest that >50% of N mineralized in sediments is lost as  $\text{N}_2$  gas and, more importantly, that most of the N input to the Galveston Bay system is removed via denitrification (~66% of the N load; 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 *in situ* and only the Zimmerman and Benner study measured rates consistently at the same stations over an annual cycle. By directly measuring denitrification rates at a series of stations over several annual cycles, we were able to obtain improved estimates of denitrification and to re-evaluate the system-level N budget for Galveston Bay.

Our study was carried out between 1996 and 1998. We measured rates of benthic metabolism and denitrification *in situ* using benthic chambers three to six times per year, optimally at bi-monthly intervals. We also determined sedimentary (grain size, pore water nutrient concentration, porosity, chlorophyll  $a$  concentration) and water column geochemical (nutrient and dissolved gas concentration, temperature, salinity, pH, chlorophyll  $a$ ) parameters. Most of the

methods used our studies of denitrification have been published previously (Joye and An 1997, 1998; An and Joye 1997; Joye et al. 1996, 1997). The objectives of the study were quantify denitrification rates 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 1998 sampling year, we worked at 4-5 stations along the Trinity River salinity gradient and at three other stations at Texas City (TC), in the East Bay (EB), and a northern station along the Houston Ship Channel (SC) (Joye and An 1998; Fig. 1). Three to six stations were sampled during the period covered by this report, November 1997 (3 stations), January 1998 (3 stations), April 1998 (6 stations), August 1998 (6 stations), and October 1998 (6 stations). During November and January 1998, sampling was limited to 3 stations because of high flow conditions (strong currents made scuba diving extremely dangerous). During August of 1998, no benthic chamber fluxes are available from the Trinity River stations because our benthic chambers were removed (after emplacement and during incubation) by some unknown person. The chambers were later recovered by the Chambers County Sheriff's department. The lack of chamber data during August 1998 is disappointing because extremely low river flow resulted in elevated salinity at our fresh water stations. During 1998, salinity at the Trinity stations varied between 0 and 12 parts per thousand (ppt), compared to 0 and 8 ppt during 1997, and 0 to 15 ppt during 1996. Four transect stations that were interspersed between the primary sampling stations were also monitored. Only surface and bottom nutrient and dissolved gas concentrations were determined at the transect stations.

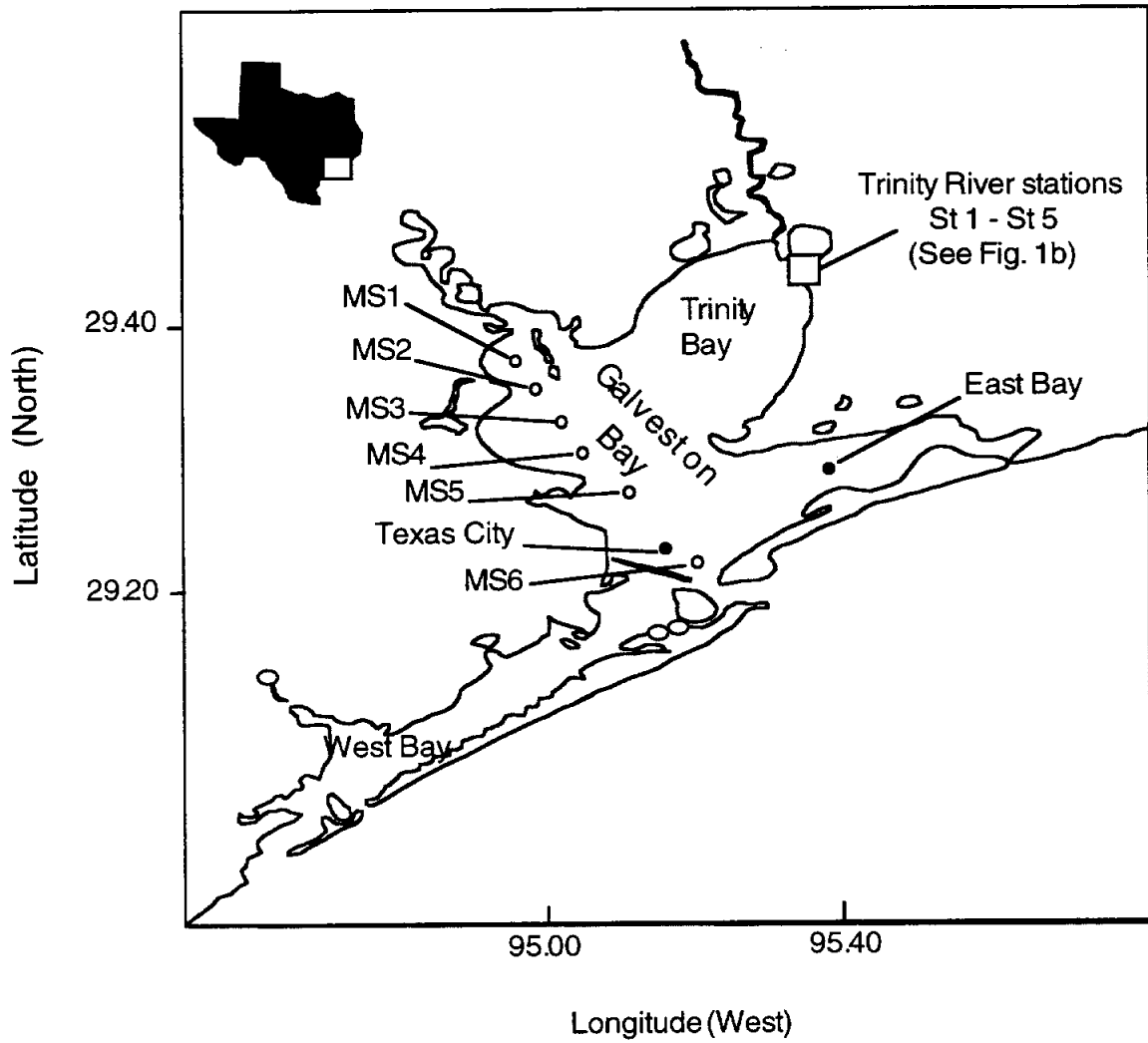


Figure 1(a). Sampling Stations in Galveston Bay. MS 1-6 represent the monitoring stations of the TNRCC. See Fig. 1b for detail map of the Trinity River chamber and transect stations.

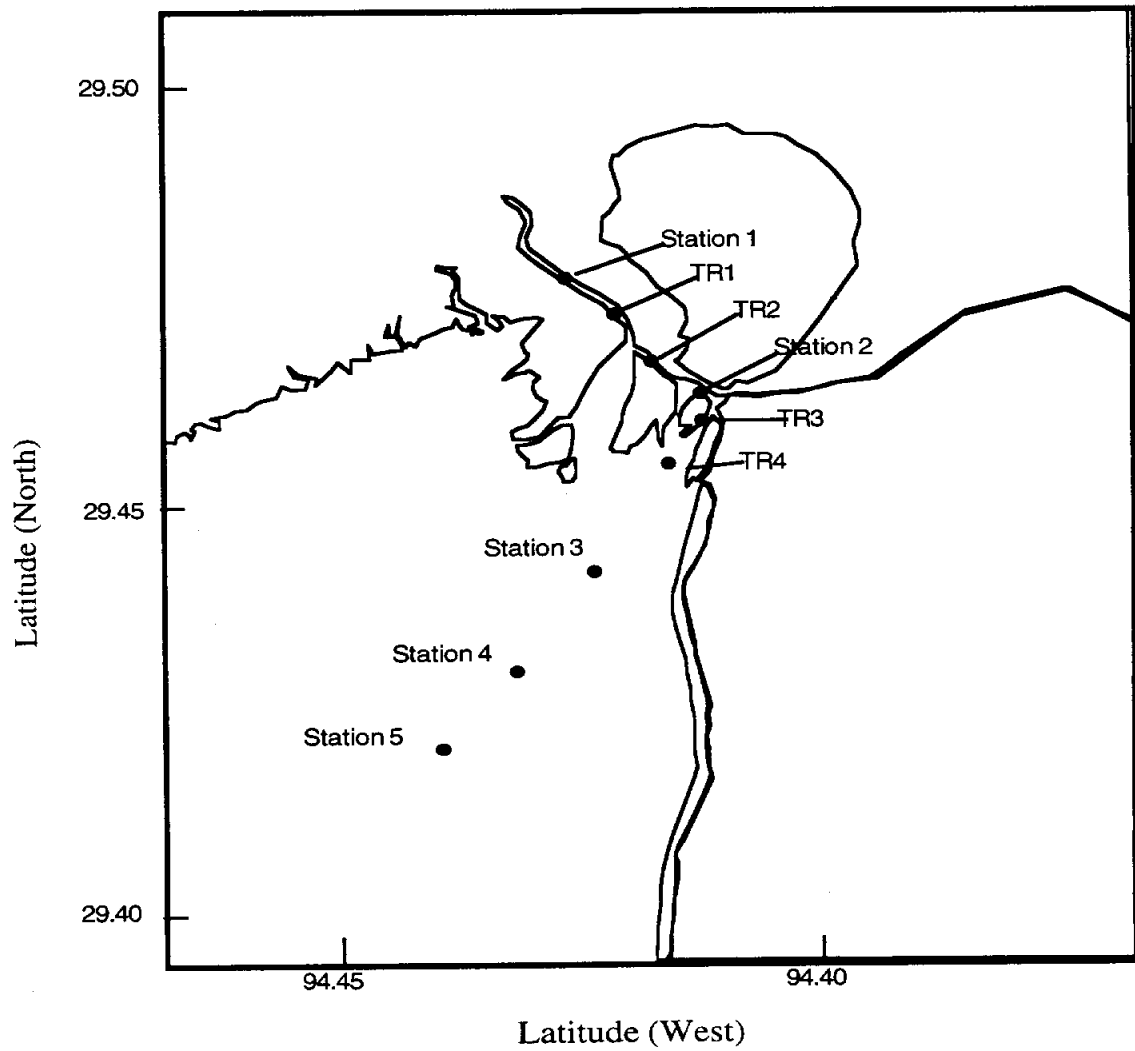


Figure 1(b). Detail map of the Trinity River chamber (stations 1-5) and transect (TR 1 - 4) stations. [Redrawn from Joye and An (1997)].

*Water column and sediment variables.* A suite of environmental variables were measured at each station. A Hydrolab DataSonde® Multiprobe was used to obtain water column profiles of temperature, salinity, pH and dissolved oxygen (O<sub>2</sub>) concentration. Samples for determining nutrient concentration were collected from ca. 0.5 m below the surface and from ca. 0.5 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 prior to nutrient analysis. NO<sub>3</sub> + NO<sub>2</sub> and PO<sub>4</sub> concentration were determined using standard methods on an Alpkem FlowSolution 3000 Autoanalyzer (Joye et al. 1999). NH<sub>4</sub> concentration was determined spectrophotometrically using the pheno-hypochlorite method (Joye et al. 1999).

Sediment cores (50 cm long and 5 cm wide) were collected by scuba divers in order to obtain profiles of pore water nutrient concentration, chlorophyll a concentration, porosity, and grain size distribution. Pore waters were collected using a Reeburg Squeezer (Joye and An 1997) which expresses pore water under a pressurized N<sub>2</sub> atmosphere. Pore water samples were 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 still being completed. Determination of chlorophyll concentration are described elsewhere (Joye and An 1998; An 1999).

Duplicate samples for porosity determination were collected at 1-5 cm intervals throughout the length of the core. Porosity was estimated from sediment

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).

*Benthic Chamber Incubation.* The protocol we used for benthic chamber incubations has been presented previously (Joye et al. 1996). Briefly, duplicate clear chambers were placed onto the sediment - water interface by a SCUBA diver. When placing chambers onto the sediment, two valves on the top of the chamber were kept open to prevent pressure buildup [which could lead to pore water extrusion] during chamber emplacement. These valves were closed after the chamber was stabilized and initial samples were collected (see below). Chambers were incubated for 24 (± 3) hours and then final samples were collected (see below).

Samples for dissolved gases and nutrients were collected as follows. Triplicate dissolved O<sub>2</sub> and N<sub>2</sub> samples were collected into gas-tight glass syringes (Glass Pak®) without introducing bubbles. Syringes were stored at 4°C until analysis via gas chromatography approximately 4 - 7 days later (An and Joye 1997). Syringes were filled with He-purged water prior to sampling to reduce the possibility of atmospheric contamination and were rinsed by drawing ca. 3 mL of sample into the syringe, dispelling that volume, and then collecting a “clean” 10 mL sample. Two larger (125 mL) syringes of water from each chamber were collected after obtaining the N<sub>2</sub>/O<sub>2</sub> samples and then the chamber valves were closed. Dissolved inorganic carbon (DIC) samples were dispensed into 10 mL vials using a canula to prevent sample degassing and/or the introduction of bubbles; vials were over-filled 2X with sample. DIC samples were fixed with

azide (0.5%), capped with teflon coated screw caps without introducing a headspace, and stored at 4° C prior to analysis via coulometric titration (Joye and An 1998). Dissolved O<sub>2</sub>, N<sub>2</sub>, and Ar concentration was quantified using gas chromatography (An and Joye 1997). Inorganic nutrient concentration was determined as described for water column and pore water samples.

### III. Results and Discussion

*Water column temperature, salinity and dissolved O<sub>2</sub> distribution.* Physico-chemical characteristics for the study sites during the 1996 - 1998 study period are presented in Table 1. The depth of the Trinity River stations varied from 1.5 to 3 m in depth. Because dredging activity is frequent in the Trinity, some stations (e.g., St. 3 between Aug and Nov 1998, see Figs. 2 and 4) exhibited dramatic short term differences in depth because of dredging. Despite the shallow depths of these stations, however, temperature stratification was frequent, with surface to bottom temperatures differing by as much as 2 °C. Temperatures at the Texas City site were similar (within 1-2 °C) to those observed at the Trinity stations. The salinity at the Trinity stations was zero, except during summer (July-August are elevated every year). During the summer of 1998, salt intrusion was observed at Station 1; this station had never exhibited elevated salinity prior to this time. Salinity at the Texas City station was lowest during January (6 - 13 ppt) and highest during summer (ca. 30 ppt). Salinity at the East Bay site was always higher than those observed at the Trinity stations but lower than those observed at Texas City (5 - 20 ppt). Dissolved O<sub>2</sub> concentration was highest during winter and at the lowest salinities (Table 1). Significant surface-bottom differences were apparent at all stations during most sampling periods (see below). Secchi depth throughout the bay averages 0.6 - 0.7 m with a range of 0.2 to 1.2 m (An 1999).



Table 1. Location and environmental parameters at sampling and transect stations 1996 - 1998.  
See Fig. 1 for the location of the transect stations.

Station Number	1		2		3		4		5		TC		EB	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
<b>Location</b>	94.43.063	94.41.511	94.42.828	94.43.667	94.44.063	94.49.659	94.44.063	94.49.659	94.44.063	94.49.659	94.44.063	94.49.659	94.44.063	94.49.659
<b>Longitude</b>	29.47.700	29.46.348	29.43.771	29.42.613	29.41.995	29.23.516	29.41.995	29.42.613	29.41.995	29.23.516	29.41.995	29.42.613	29.41.995	29.23.516
<b>Latitude</b>	2.1	3	3.6	1.5	1.5	4.5	1.5	3.6	1.5	4.5	1.5	3.6	1.5	4.5
<b>Depth (m)</b>	28	28	28.5	27	28.5	28.2	28.5	27	28.5	28.2	28.5	27	28.5	28.2
<b>Temp. (°C)</b>	31.3	30.6	30.5	27.5	31	-	30.5	27.5	31	-	30.5	27.5	31	-
	28.3	28	28	26.9	28.5	28	28.2	26.9	28.5	28	28.2	26.9	28.5	28
	-	-	-	-	18.5	17	-	-	18.5	17	-	-	18.5	17
	14.3	14.3	14	14.1	13.8	13.8	14	14.1	13.8	13.8	14	14.1	13.8	13.8
	18.7	18.7	20.1	19.9	18.9	18.7	20.1	19.9	18.9	18.7	20	19.7	18.9	18.7
	30.6	30.6	32.8	32.8	29.6	29.6	32.8	32.8	29.6	29.6	31.4	31.2	32.8	31.2
	31.6	30.7	27.9	26.9	31.6	31.6	27.9	26.9	31.6	31.6	31.1	31	31.6	30.8
	15.6	15.6	15.4	15.3	12.9	12.9	15.4	15.3	12.9	12.9	-	-	15.6	15.6
	14.5	-	14.3	14.4	14.1	14.2	14.3	14.4	14.1	14.2	-	-	14.5	15.2
	32	31.7	31.2	30.4	31.8	31.2	31.2	30.4	31.8	31.2	33.2	31.1	30.2	30.8
	21.7	21.8	21.9	21.6	22.2	20.1	21.7	21.6	22.2	20.1	21.9	21.7	22.1	22.1
<b>Salinity (ppt)</b>	0	0	10	12	15	-	0	12	15	-	16	17	-	-
	0	0	0	0	-	-	0	0	-	-	-	-	-	-
	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	1.5	1.5	0	0	1.5	1.5	6.3	7.2	0	0
	0	0	0	0	0	0	0	0	0	0	0.9	1.2	0	0
	0	0	0	0	0.4	0.4	0	0	0.4	0.4	20.9	23.8	0	0
	0	0	3.3	4.1	5.2	5.3	4.1	4.1	5.2	5.3	7.6	7.8	29.6	29.6
	0	0	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	-	-	6	6
	0	0	0	0	0	0	0	0	0	0	-	-	13	13
	3.93	3.95	11.18	11.93	12.22	12.18	11.18	11.93	12.22	12.18	28.2	31.3	19.9	20.4
	0	0	0	0	1.6	5.8	0	0	1.6	5.8	4.6	6.4	13.7	11.3
	9.8	6.5	9.1	6.6	7.7	6.1	9.1	6.6	7.7	6.1	-	-	-	-
	7.2	6.4	5.0	4.2	-	6.6	5.0	4.2	-	6.6	-	-	-	-
	6.8	5.2	5.4	7.5	8.6	5.8	5.4	7.5	8.6	5.8	-	-	-	-
	-	-	-	-	8.7	7.9	-	-	8.7	7.9	8.4	6.2	-	-
	10.2	10	10	10.2	10.2	10.2	10	10.2	10.2	10.2	9.2	8.5	-	-
	7.7	7.6	8.3	7.9	8.3	8.2	8.3	7.9	8.3	8.2	8.3	7.8	-	-
	6.8	5.6	6.7	6.3	6.2	6.6	6.7	6.3	6.2	6.6	7.1	5.7	-	-
	7.3	4.6	6.7	6.4	7.5	7	6.7	6.4	7.5	7	5.5	5	8.9	6.5
	9.8	9.3	9.1	9.1	9.8	9.6	9.1	9.1	9.8	9.6	-	-	-	-
	10	9.9	10.2	10.2	10.5	10.5	10.2	10.2	10.5	10.5	9.5	8.7	-	-
	6.7	5.4	5.2	3.6	5.9	5.6	5.2	3.6	5.9	5.6	6.4	6.3	6.6	5.5
	6.6	6.0	6.3	6.2	7.1	5.6	6.3	6.2	7.1	5.6	7.4	5.9	8.2	7.3

Table 1 (Continued)

Location	Longitude Latitude	OB Surface Bottom	Transect Station							
			1 Surface Bottom	2 Surface Bottom	3 Surface Bottom	4 Surface Bottom				
Depth (m)	Temp. (°C)	94.50.87	94.42.551	94.42.275	94.41.479	94.41.991				
		29.16.91	29.47.41	29.46.907	29.45.947	29.44.864				
		5.1	3.6	3.6	3.6	3				
	1996	June	-	-	28	28	-	-	-	-
		July	-	31	31.5	30.5	31.5	32	31.1	28.2
		Aug.	28	27.2	-	-	-	-	-	27
	1997	Oct.	23	22.5	-	-	-	-	-	-
		Jan.	-	14.3	14.3	14.2	14.3	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
		Nov.	-	15.5	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
		Apr.	-	-	-	-	-	-	-	-
		Aug.	-	32.4	32.2	32.2	32	31.3	30.1	32
		Nov.	-	21.8	21.8	21.9	21.8	21.8	21.8	21.8
Salinity (ppt)	1996	June	-	-	-	3	-	-	-	0
		July	32	34	-	0	-	-	-	10
		Aug.	-	-	-	-	-	-	-	-
	1997	Oct.	-	-	-	-	-	-	-	-
		Jan.	-	0	0	0	0	0	0	0
		Apr.	-	-	-	-	-	-	-	-
		July	-	0	0	0	0	0	0	0
		Aug.	-	0	0	0	0	0.4	2.7	1.1
		Nov.	-	0	0	0	0	0	0	0
	1998	Jan.	-	0	0	0	0	0	0	0
		Apr.	-	-	-	-	-	-	-	-
		Aug.	-	3.12	3.13	3.54	3.6	6.54	8.78	9.38
		Nov.	-	0	0	0	0	0	0	0
O <sub>2</sub> (m/L)	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
		Aug.	10.2	4.3	-	-	-	-	-	3.9
		Oct.	8.2	4.2	-	-	-	-	-	7.6
	1997	Jan.	-	10.3	9.8	10.3	9.5	10.1	9.8	10.3
		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
		Nov.	-	10	9.5	9.2	9	9.2	9	9
	1998	Jan.	-	9.8	9.7	10.1	10.1	9.7	9.7	9.6
		Apr.	-	-	-	-	-	-	-	-
		Aug.	-	6.0	5.1	5.6	5.2	5.0	3.6	6.1
		Nov.	-	6.7	6.3	7.1	6.3	6.9	6.4	6.7

The depth distribution of temperature, salinity, pH and dissolved O<sub>2</sub> appears to be a function of freshwater inflow rate, particularly in the Trinity River region. Water column stratification is apparent and significant during periods of low flow (August), but is less significant during periods of high flow (November) (Fig. 2-5). The depth distribution of temperature, salinity, pH and dissolved O<sub>2</sub> at all stations in August, a period of extremely low flow, is shown in Figs. 2 and 3. Depth variation in temperature, salinity, pH and dissolved O<sub>2</sub> are apparent at more saline stations (Fig. 2A-C) but no obvious depth trends in pH occur. Along the Trinity River stations, subtle gradients in temperature and salinity create a stable water column and generate significant O<sub>2</sub> depletion at depth, particularly at mid-River sites (Fig. 2 G-I; Fig. 3). Dissolved O<sub>2</sub> % saturation varied between 45 and 100% and was as low as 45% at the mid-river stations (Fig. 3). These low concentrations of dissolved O<sub>2</sub> resulted in dramatic changes in nutrient distributions (see below). As reported previously, only a slightly stratified water column is required to generate strong chemical stratification with respect to dissolved O<sub>2</sub> concentration (Joye and An 1998).

The depth distribution of temperature, salinity, pH and dissolved O<sub>2</sub> during November, a period of high river flow, is shown in Figs. 4, 5 and 6. As observed in August, depth variation of salinity and dissolved O<sub>2</sub> was significant at the Texas City station (where a halocline was present) but not at the East Bay station (which had no halocline) (Fig. 4A & C). Depth trends in pH and temperature were weak. Along the Trinity River, no water column gradient in temperature or salinity was observed at Stations 1 through 3 (Fig. 4 D-J); however, changes in dissolved O<sub>2</sub> concentration were still apparent even though they were much less dramatic compared to those observed in August. At Stations 4 and 5, a water column halocline was present and the change in dissolved O<sub>2</sub> over

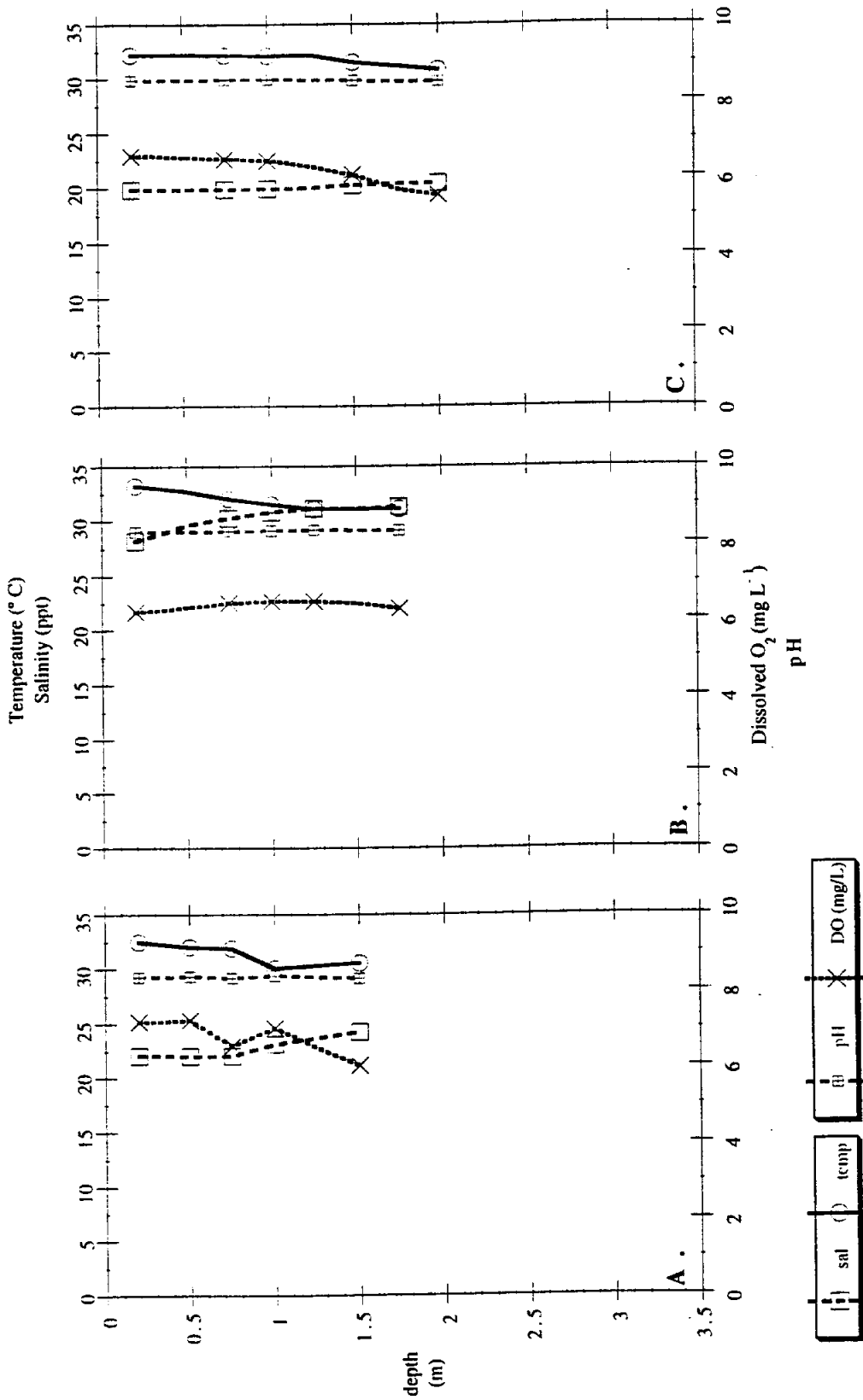
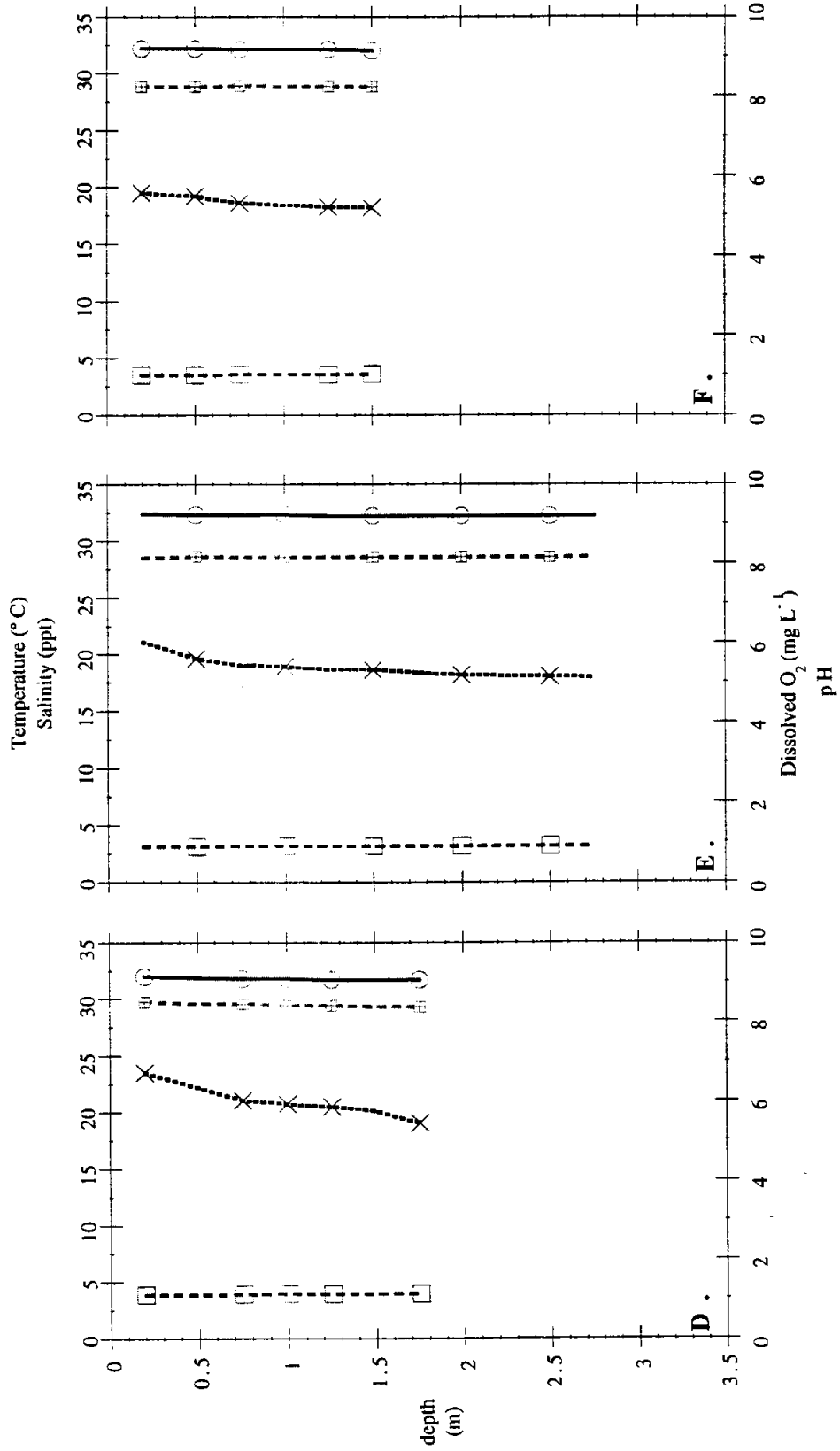
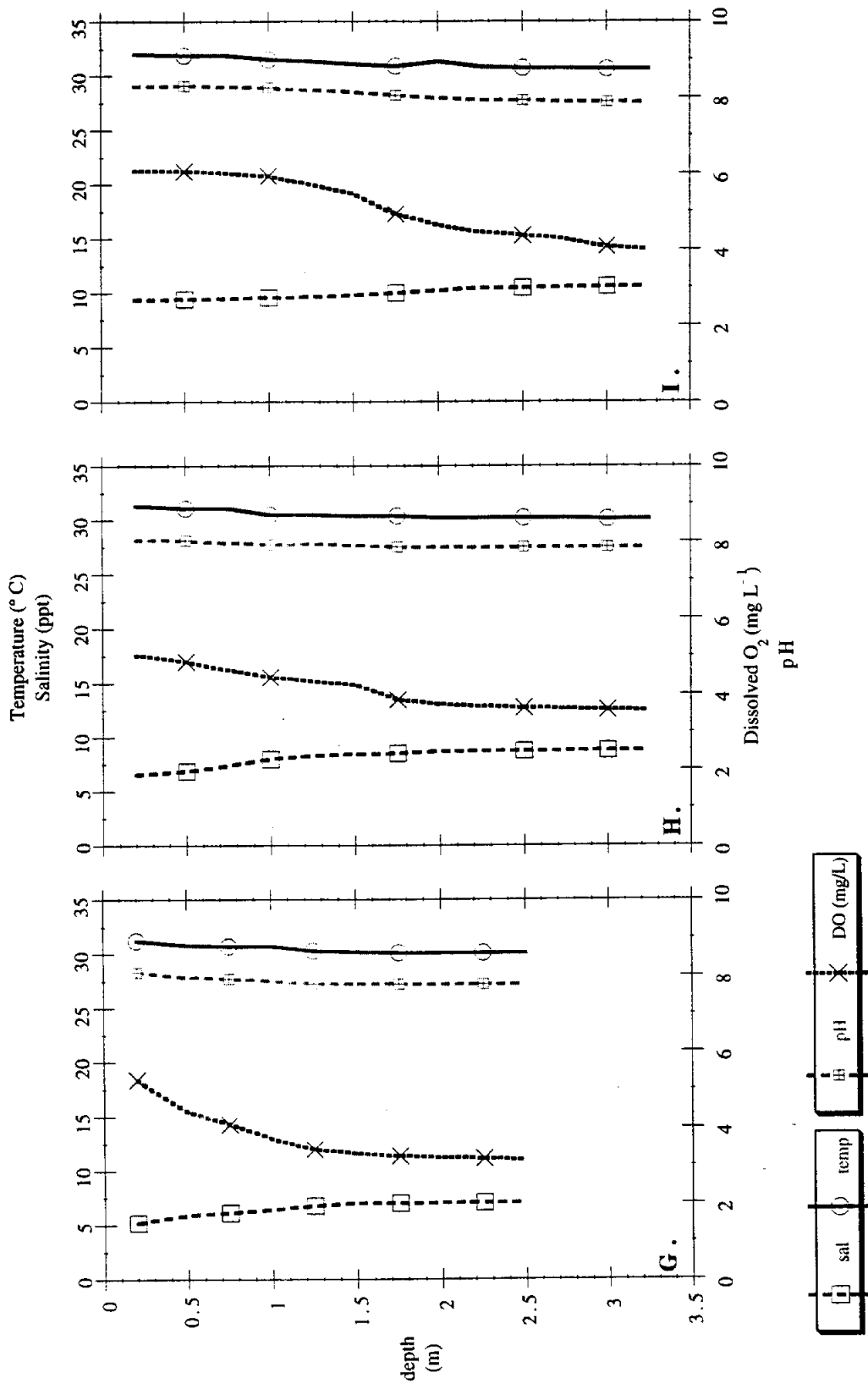
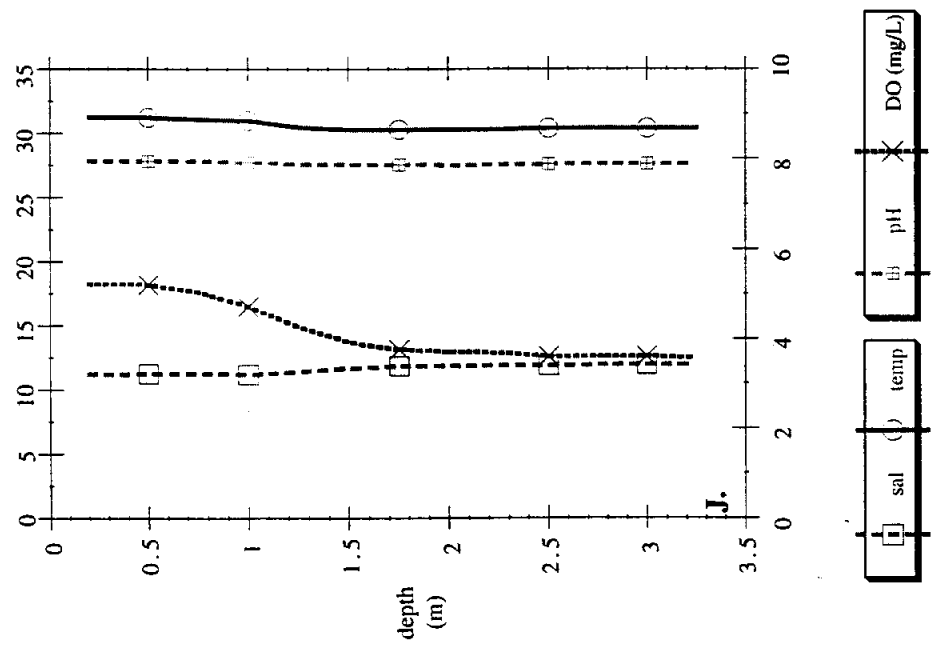
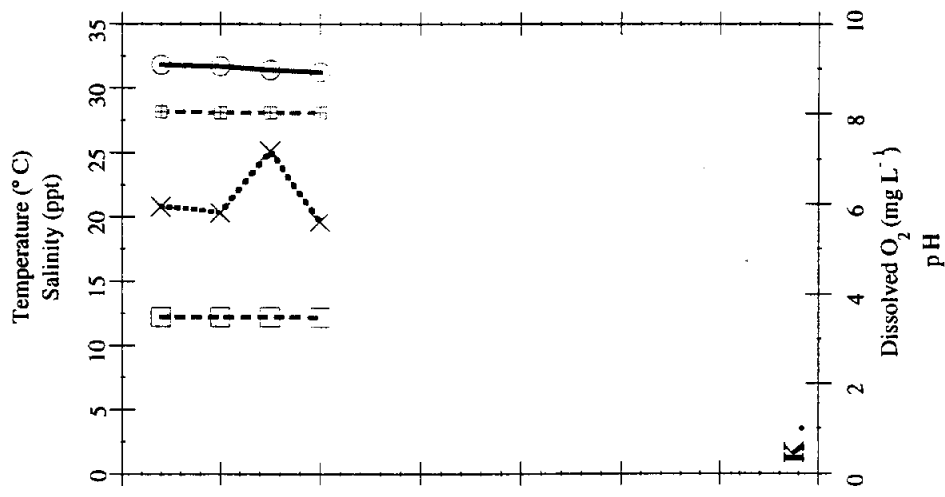


Figure 2: Depth profiles of temperature (○) and salinity (□) [upper axis] and dissolved O<sub>2</sub> (×) and pH (□) [lower axis] during August 1998. Stations are listed as follows: A: Texas City; B: Ship Channel; C: East Bay; D: Sta. 1; E: TR 1; F: TR 2; G: Sta. 2; H: TR 3; I: TR 4; J: Sta. 3; K: Sta. 4. Symbols are consistent on panels A-K.







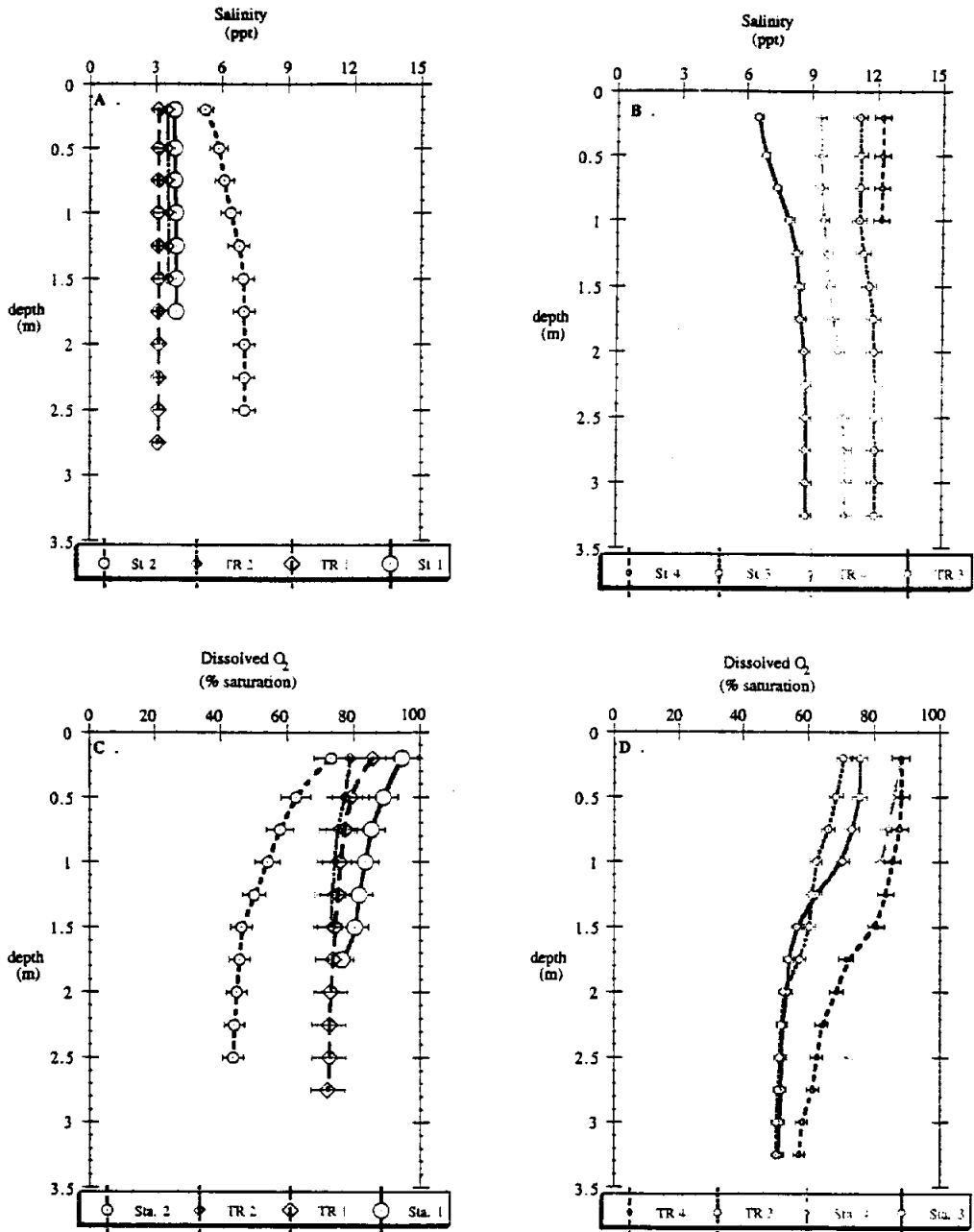


Figure 3: Depth profiles of salinity (A, B) and dissolved O<sub>2</sub> (C, D) along Trinity River salinity gradient stations in August 1998. Station identifications are provided in the figure legend.



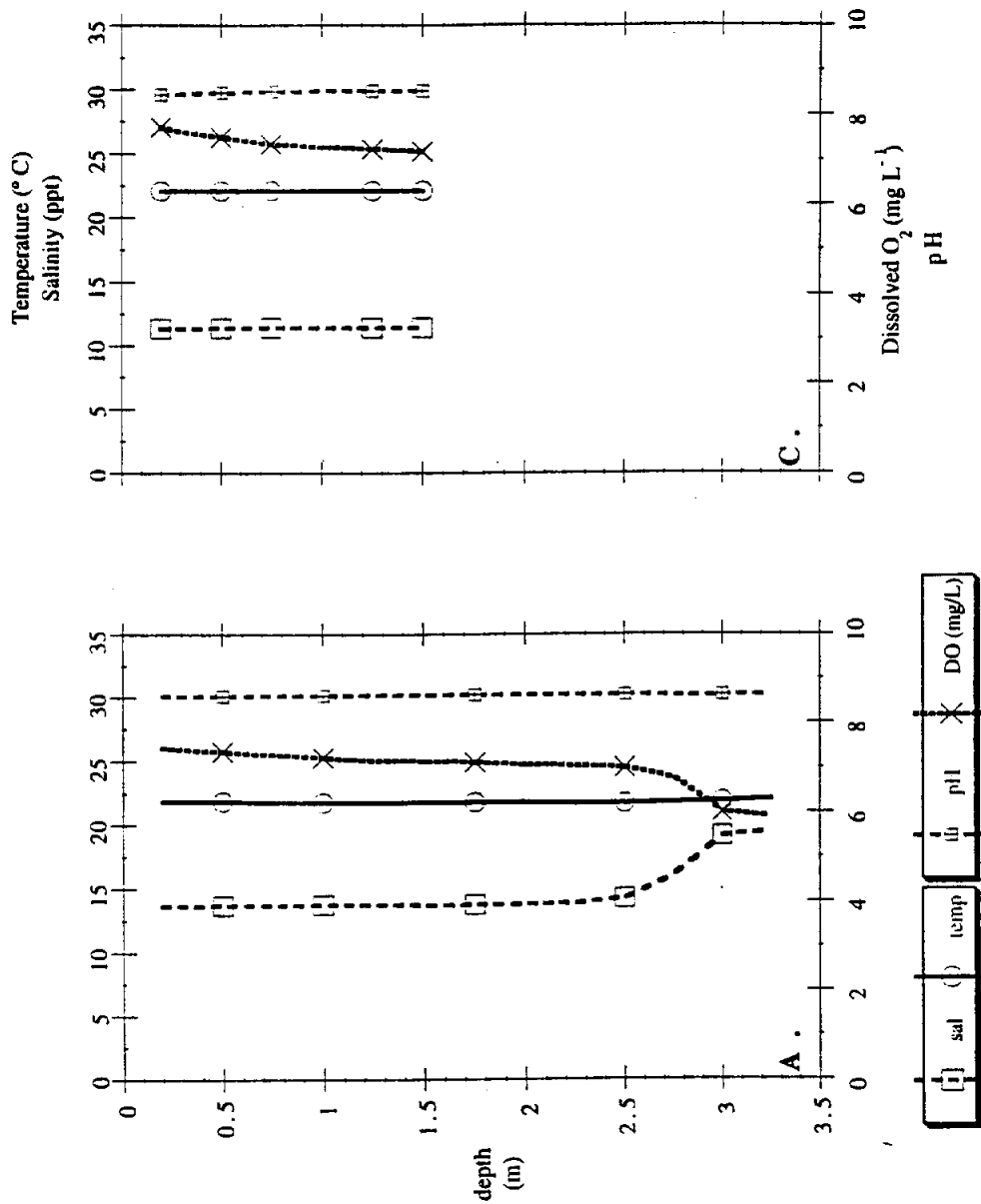
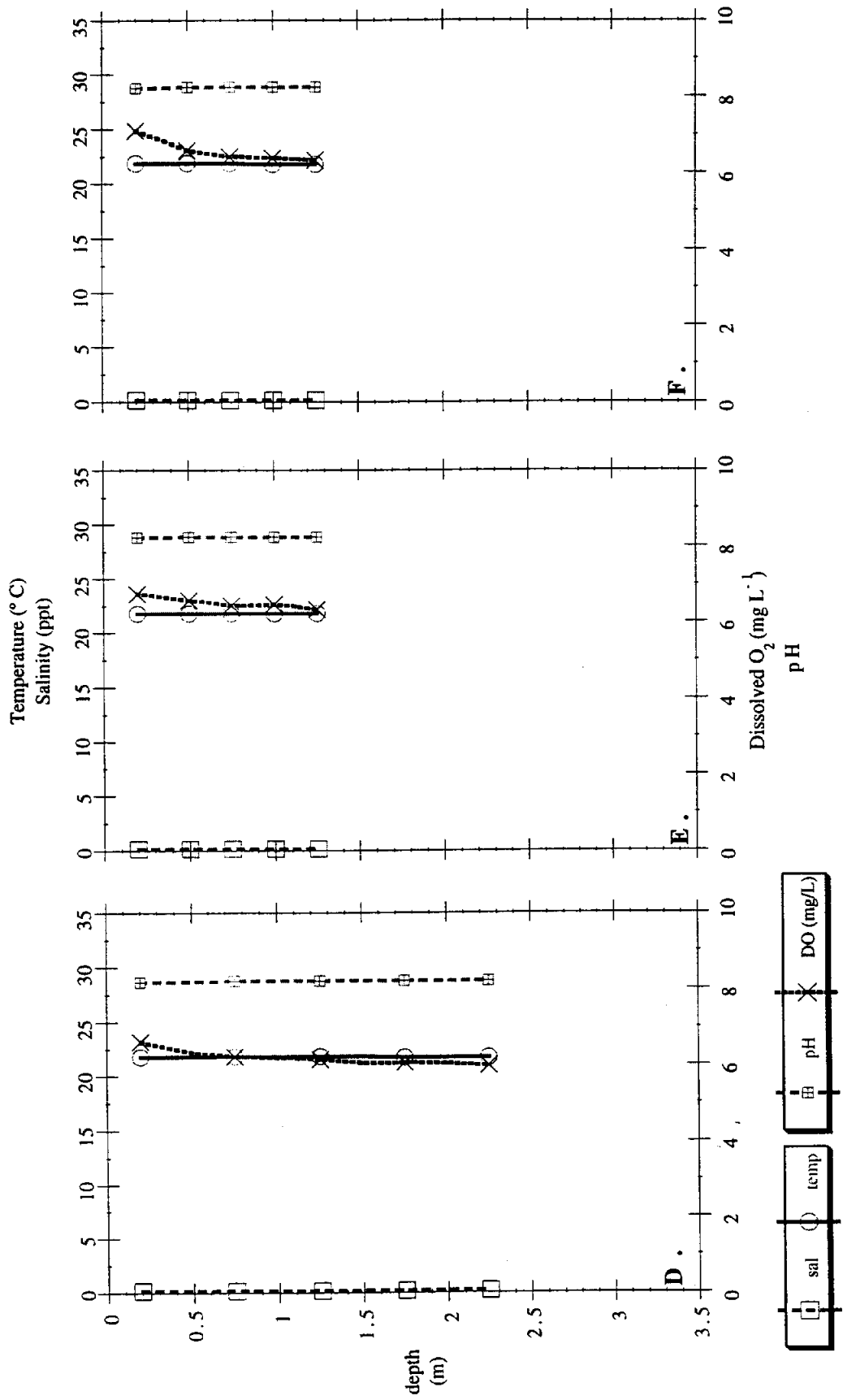
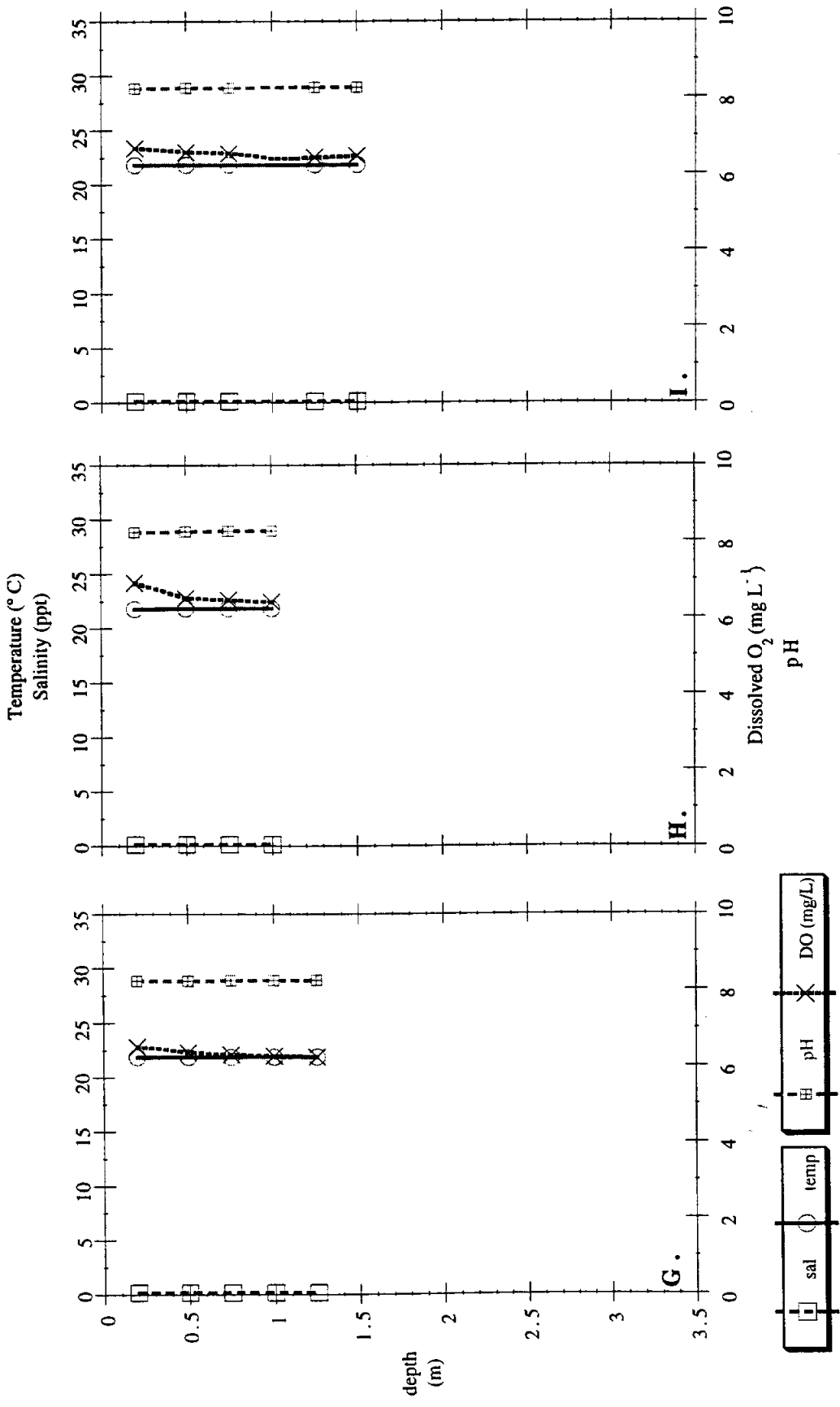
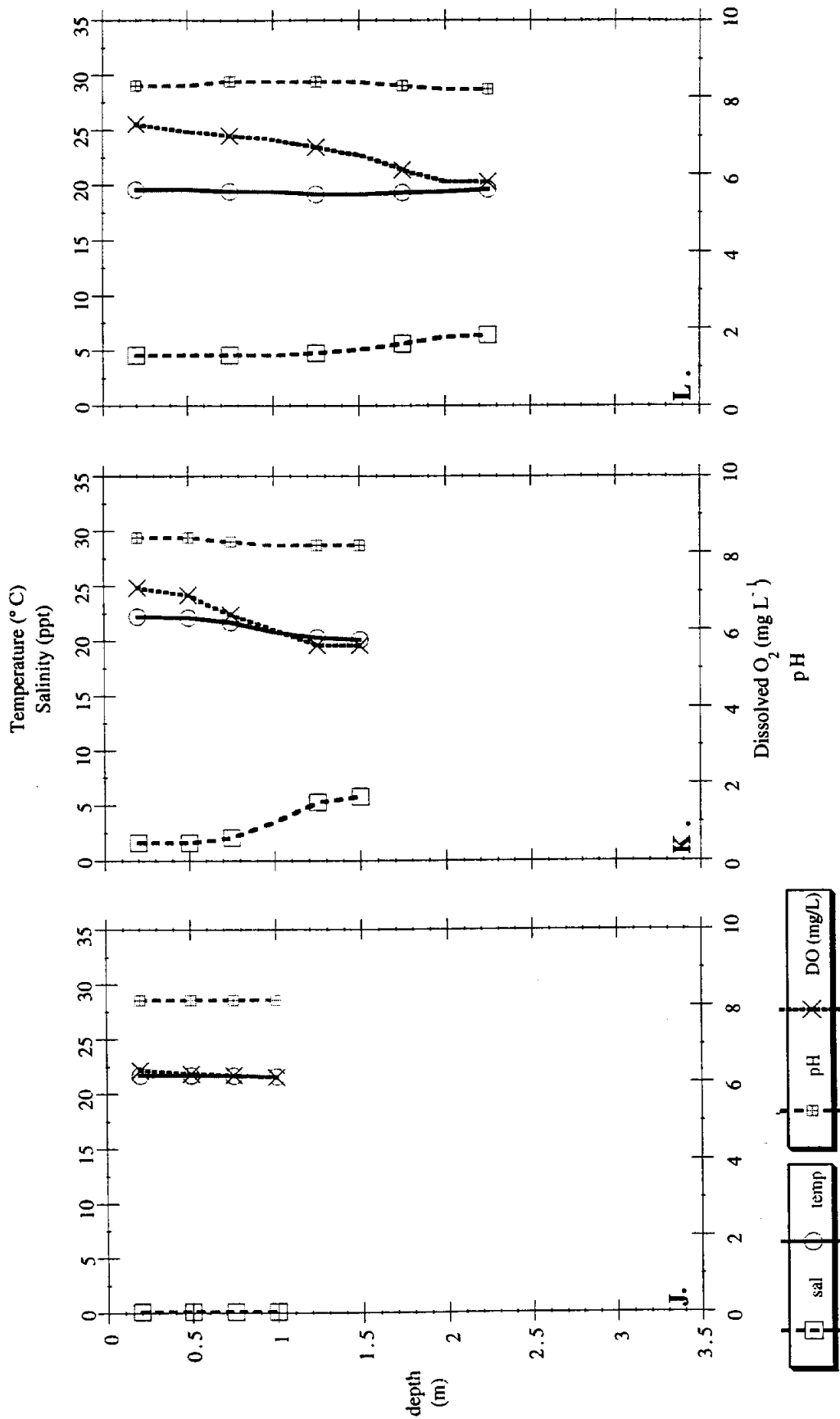


Figure 4: Depth profiles of temperature (○) and salinity (□) [upper axis] and dissolved O<sub>2</sub> (×) and pH (□) [lower axis] during November 1998. Stations are listed as follows: A: Texas City; C: East Bay; D: Sta. 1; E: TR 1; F: TR 2; G: Sta. 2; H: TR 3; I: TR 4; J: Sta. 3; K: Sta. 4; L: Sta. 5. Symbols are consistent on panels A-L.







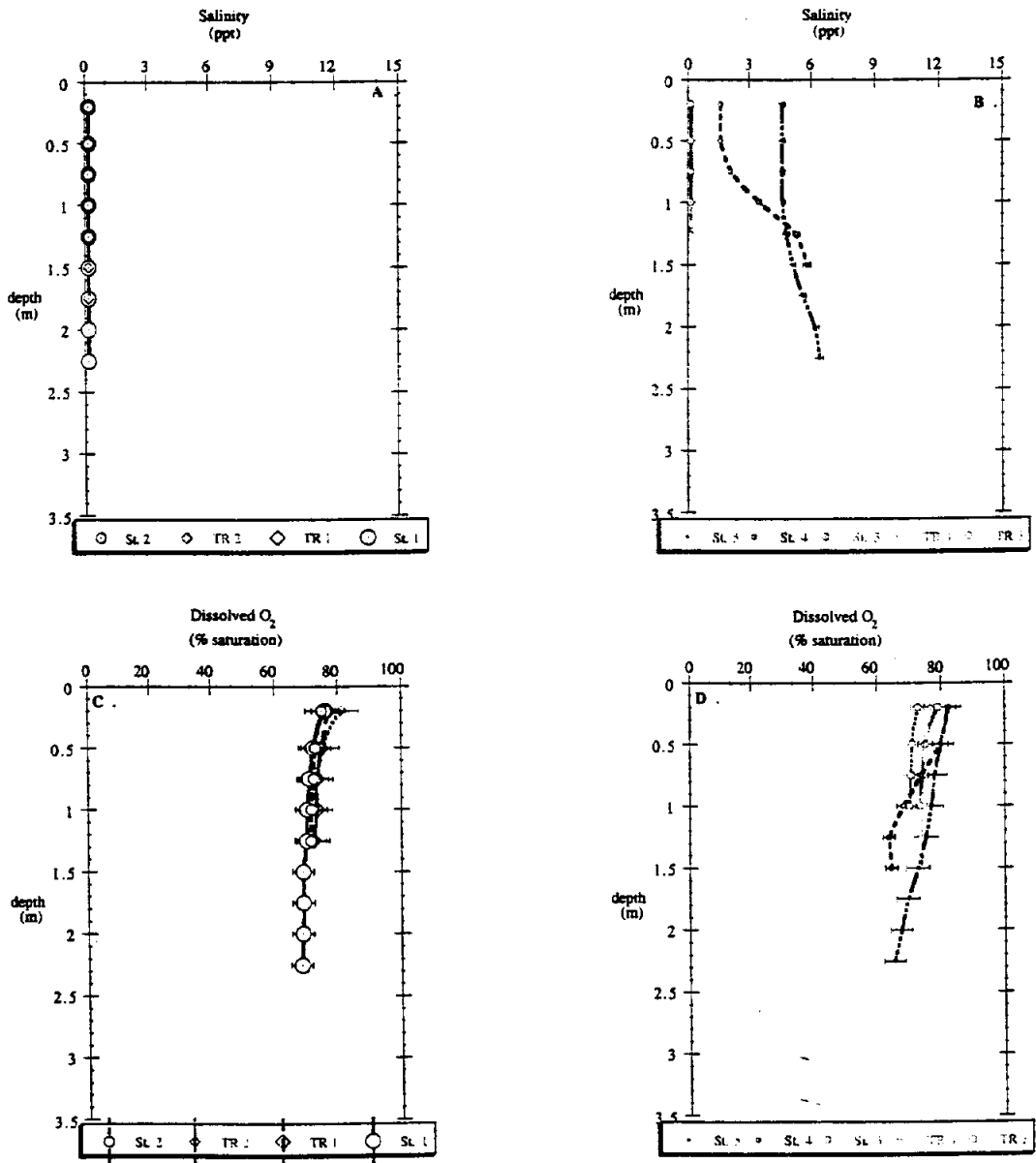


Figure 5: Depth profiles of salinity (A, B) and dissolved O<sub>2</sub> (C, D) along Trinity River salinity gradient stations in November 1998. Station identifications are provided in the figure legend.

depth was more significant (Fig. 4 K, L). At this time, salinity variation in the water column appeared to generate most of the stability that generates changes in dissolved O<sub>2</sub>. Dissolved O<sub>2</sub> % saturation varied between 70 and 80 % in the upper Trinity (St. 1, 2 and TR 1, 2) and at stations with 0 salinity (TR 3, 4, and St. 3) (Fig. 5). Dissolved O<sub>2</sub> % saturation varied between 60 and 80 % in the more saline stations (St. 4 and 5) (Fig. 5). As mentioned previously, dissolved O<sub>2</sub> % saturation was correlated with salinity at the most saline stations, Texas City and the East Bay (Fig. 6).

Both temperature and salinity appear to contribute to water column stability and thus generate reductions of dissolved O<sub>2</sub> concentration at depth. Temperature-salinity patterns are driven, primarily, by variations in freshwater inflow rate, tidally-induced mixing of the water column, and wind-mixing of the water column. During periods of low freshwater inflow and reduced turbulent mixing, biological activity generates chemical gradients even in the presence of modest thermal or salinity stratification. The most profound decreases in dissolved O<sub>2</sub> concentration were observed in August 1998 (Fig. 7A). The lowest dissolved O<sub>2</sub> concentration were observed at St. 2, TR 3 and TR 4; these surface to bottom changes reflected a 40% decrease in dissolved O<sub>2</sub> inventory over a 2 m water column (Fig. 7B). Twenty percent reductions in dissolved O<sub>2</sub> concentration were observed at Stations 4 and 5 in October of 1998 (Fig. 7B). The high O<sub>2</sub> demand apparent from these O<sub>2</sub> profiles in the Trinity mid-river stations during August of 1998 are particularly noteworthy. Reduced freshwater inflows resulted in salinity intrusions past our most 'fresh' station (St. 1). At the midpoint of our Trinity River transect, the bottom water oxygen concentration was low, approaching hypoxic ( $=2 \text{ mg O}_2 \text{ L}^{-1}$ ) conditions. Marked effects on water column nutrient distributions were observed (see below). This pattern suggests that

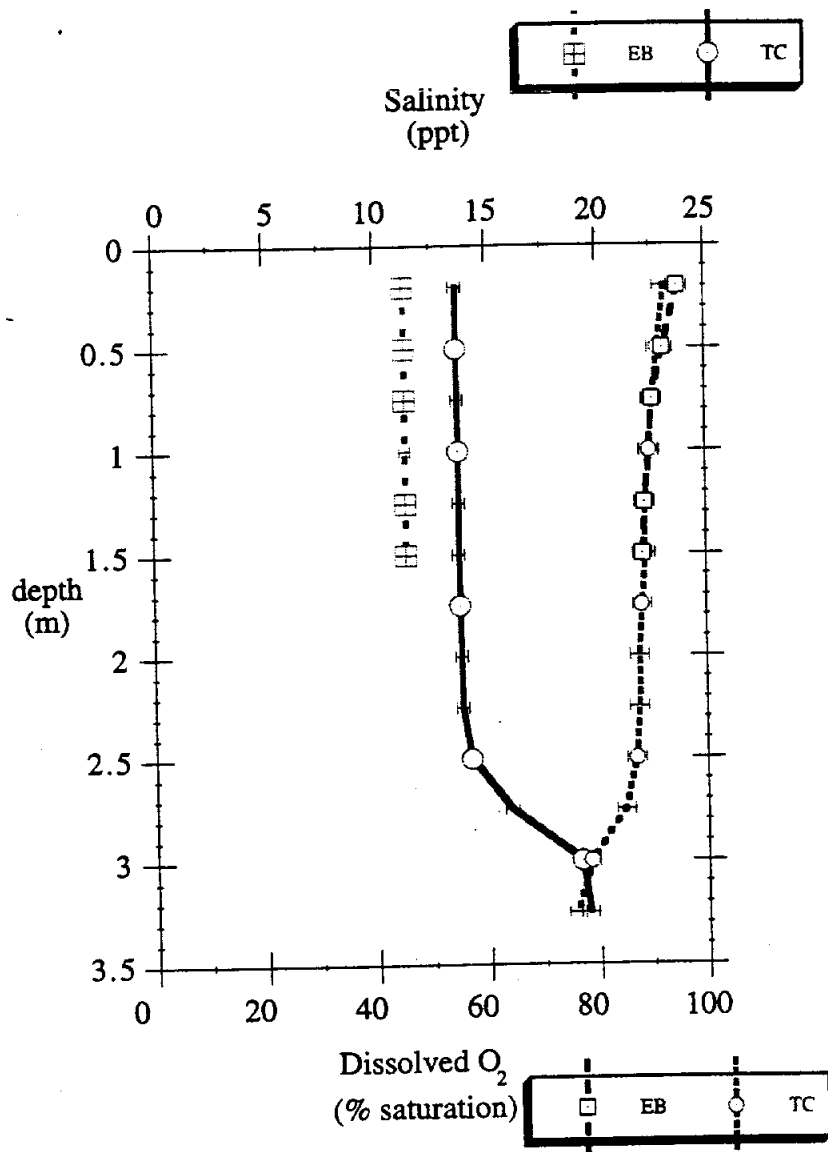


Figure 6: Depth profiles of salinity (upper axis) and dissolved O<sub>2</sub> (lower axis) at Texas City and East Bay stations in November 1998. Station identifications are provided in the figure legend.

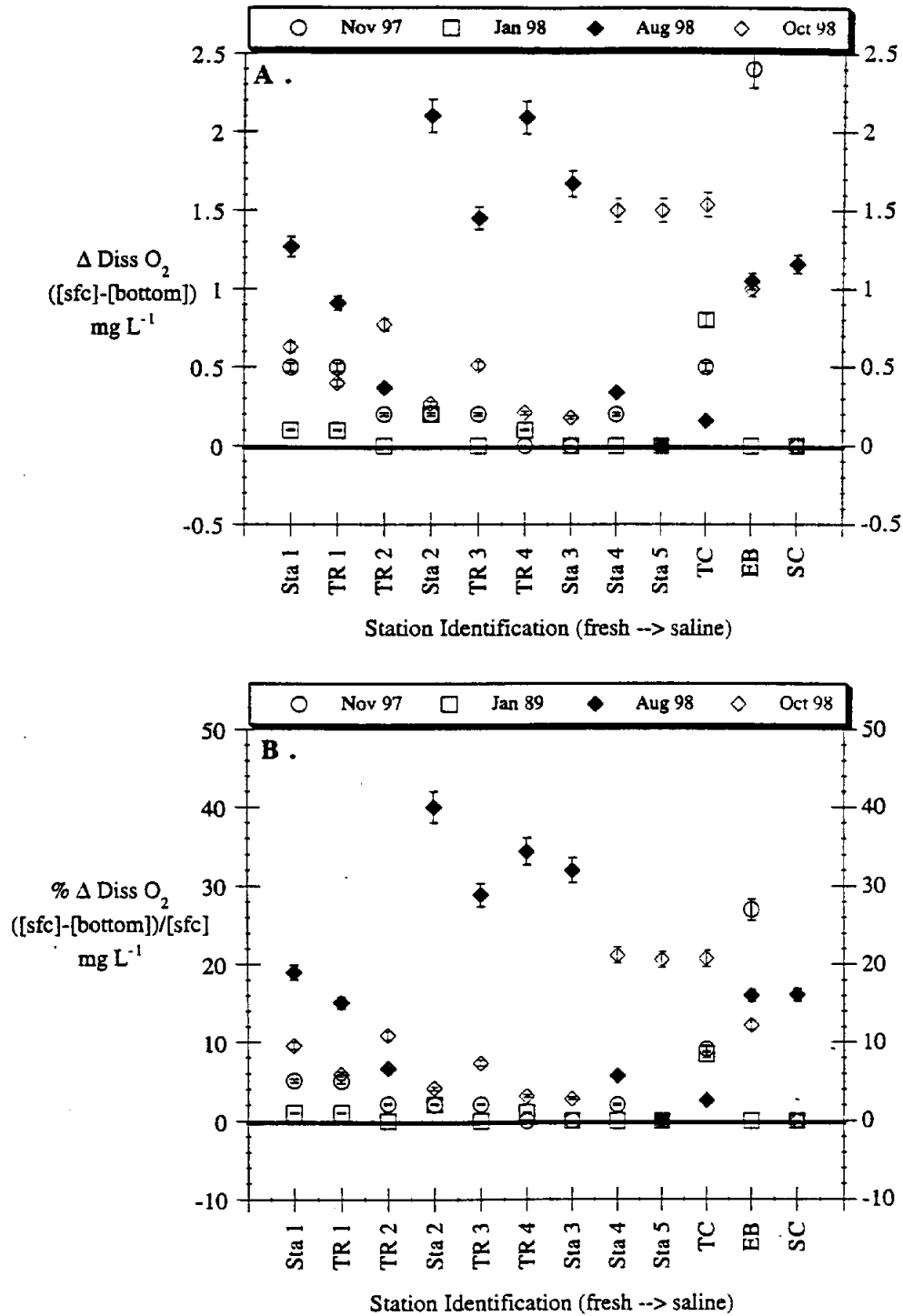


Figure 7: Difference in dissolved O<sub>2</sub> concentration over depth at all stations (X axis) between Nov. 1997 and Oct. 1998. Panel (A) illustrates the difference in concentration (mg L<sup>-1</sup>) between surface and bottom stations (i.e., surface concentration – bottom concentration). Panel (B) illustrates the percent change over depth (i.e., [(Δ concentration / surface concentration)\*100]). Date identifications are provided in the figure legend.



reductions in fresh water inflow, whether they arise from increased municipal, agricultural, or industrial exports or from a natural drought, will have deleterious effects on nutrient and materials cycling in the river, particularly if they occur during summer months. Though we have no benthic flux data at this time for the Trinity stations (see methods for explanation), changes in water column nutrient concentrations and sediment pore water inventories suggest that benthic metabolic rates were indeed altered.

During the summer months, rates of microbial processes in the sediment and water column are elevated due to increased temperatures. Increasing salinities (because of decreased freshwater inflow) along with seasonal highs in temperature promote stratification of the water column. High rates of benthic metabolism in this situation can result in O<sub>2</sub> depletion of bottom waters. Furthermore, when low O<sub>2</sub> water overlies a sediment, ammonium and phosphorus remineralization are stimulated. The lack of O<sub>2</sub> limits coupled nitrification-denitrification, which increases net N regeneration rates. Low O<sub>2</sub> also increases rates of reductive dissolution of iron oxyhydroxides, which effectively increases phosphorus recycling. Enhanced sediment recycling of N and P and elevated rates of flux to the water column could stimulate water column production which will, in turn, stimulate water column and benthic respiration, exacerbating the problem. Low O<sub>2</sub> conditions also increase mobilization rates of heavy metals (Cu, Zn). Additional negative impacts of low O<sub>2</sub> conditions in river water include reductions in biomass of sediment infauna (many invertebrates cannot tolerate low O<sub>2</sub> conditions for prolonged periods of time), fish kills, and harmful algal blooms.

*Water column nutrient concentration.* Water column nutrient concentrations varied between different stations in Galveston Bay as well as between surface and

bottom samples (Table 2). In November of 1997, concentrations of ammonium ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ) and phosphate ( $\text{PO}_4$ ) were low (1-6  $\mu\text{M}$ ) and similar between surface and bottom waters. Nitrite ( $\text{NO}_2$ ) concentration was always low ( $< 0.5 \mu\text{M}$ ) and invariable from St. 1 to 4.  $\text{NH}_4$  and  $\text{PO}_4$  concentration increased slightly between St. 1 and 4 while  $\text{NO}_3$  concentration varied between stations. Lower  $\text{NO}_3$  concentration in St. 4 bottom water suggest consumption at depth (Fig. 8A, B). During periods of high freshwater inflow (Jan, Apr, Oct 1998),  $\text{NO}_3$  concentration in surface and bottom waters are elevated (Fig. 8 C – F, G & H).  $\text{NO}_3$  is the dominant inorganic nutrient form during high flow periods, being almost 10 times more abundant than  $\text{NH}_4$ ,  $\text{NO}_2$  and  $\text{PO}_4$ . Phosphate concentrations are  $\sim 1\text{-}2 \mu\text{M}$  during periods of high flow. Uptake of  $\text{NO}_3$  and production of  $\text{NH}_4$  are apparent at higher salinity stations even during high flow (Fig. 8 E, F). During August of 1998, water column  $\text{NH}_4$  concentration was the highest we observed during this 3-year study. Bottom water concentrations were significantly higher than surface water concentrations (Fig. 8 G, H) and the highest  $\text{NH}_4$  concentrations were observed at the Trinity mid-rivers stations, which exhibited the lowest bottom water dissolved  $\text{O}_2$  concentration (Fig. 7, Fig. 8 G, H).  $\text{NH}_4$  concentration was also elevated in East Bay bottom water during Aug. 1998 (Table 2). During November 1998, increased freshwater flow resulted in elevated  $\text{NO}_3$  concentrations, particularly at the freshwater sites (Fig. 8 I, J). Uptake of  $\text{NO}_3$  in bottom waters was apparent (bottom water concentration was less than surface water conc.) in freshwater stations while bottom waters  $\text{NO}_3$  production was suggested at Sta. 5 (Fig. 8 I, J).  $\text{NH}_4$  production and flux from sediments (see below) resulted in increased bottom water concentration in Sta. 3, 4 and 5 in Trinity Bay as well as at Texas City and East Bay sites. Bottom water  $\text{PO}_4$  concentration was highest at Sta. 5, possibly resulting from high rates of benthic metabolism and release of  $\text{PO}_4$  to the water column.

Table 2. Surface and Bottom Nutrient Concentrations

Sta.	Date	Surface Water				Bottom Water			
		Ammonia	Nitrite	Nitrate	Phosphate	Ammonia	Nitrite	Nitrate	Phosphate
<b>Nov-97</b>									
<i>St 1</i>		1.50	0.18	3.90	1.10	3.24	0.34	4.30	1.48
<i>St 3</i>		3.06	0.29	3.40	2.06	3.60	0.14	5.56	2.22
<i>St 4</i>		4.50	0.11	6.29	3.96	5.31	0.16	3.50	2.61
NO DATA FOR TRANSEC STATIONS IN NOV. 1997									
<b>Jan-98</b>									
<i>TC</i>		0.00	1.38	22.73	0.88	0.00	0.93	18.93	1.23
<i>St 1</i>		0.09	1.08	48.35	0.15	0.00	n. d.	n. d.	n. d.
<i>St 2</i>		0.51	1.16	46.16	0.10	0.00	1.14	46.41	0.13
<i>St 3</i>		0.00	0.92	36.03	0.10	0.05	0.91	34.23	0.15
<i>St 4</i>		0.00	0.99	38.21	0.10	0.00	0.96	37.88	0.35
TR 1		0.00	0.88	48.20	1.53	0.00	1.02	45.70	0.15
TR 2		0.77	0.98	47.51	1.10	2.77	0.93	46.42	0.15
TR 3		0.00	1.10	31.81	0.80	0.20	1.02	34.88	0.10
TR 4		4.51	1.01	46.40	0.68	0.09	1.06	48.21	0.65
<b>Apr-98</b>									
<i>TC</i>		3.37	0.849	6.30	0.70	4.75	0.44	2.60	1.55
<i>EB</i>		2.20	0.674	1.63	0.75	7.82	0.83	21.56	0.00
<i>St 1</i>		4.18	0.808	45.66	2.20	0.00	0.45	43.99	1.81
<i>St 2</i>		1.18	0.636	45.03	1.83	0.00	0.581	44.75	1.74
<i>St 3</i>		2.27	0.683	43.43	2.01	1.60	0.37	44.55	1.30
<i>St 4</i>		11.07	0.824	41.59	2.58	n. d.	n. d.	n. d.	n. d.
TR 1		0.00	0.535	44.21	1.55	0.00	0.614	43.67	1.80
TR 2		0.40	0.491	44.02	1.69	3.00	0.580	44.47	1.85
TR 3		1.20	0.536	44.72	1.87	1.40	0.624	45.83	1.87
TR 4		1.20	0.492	44.76	1.86	2.25	0.564	45.26	1.91
<b>Aug-98</b>									
<i>TC</i>		1.27	0.26	0.00	0.31	3.00	0.80	1.25	0.00
<i>EB</i>		3.98	0.36	0.00	1.61	13.00	0.38	0.40	1.70
<i>SC</i>		0.99	0.32	0.00	2.39	1.15	0.60	1.55	1.30
<i>St 1</i>		1.91	0.33	0.00	1.14	2.00	0.35	0.00	1.20
<i>St 2</i>		2.99	0.34	0.09	0.90	15.85	0.47	0.50	1.02
<i>St 3</i>		5.52	0.40	0.00	1.20	2.12	0.49	0.45	1.47
<i>St 4</i>		1.24	0.42	0.00	1.83	8.62	0.32	0.00	1.55
TR 1		0.64	0.33	0.00	0.86	2.29	0.36	0.00	0.86
TR 2		0.99	0.29	0.00	1.00	3.45	0.43	0.13	1.33
TR 3		3.24	0.39	0.25	1.10	7.49	0.38	0.63	1.46
TR 4		2.65	0.35	0.00	1.40	15.08	0.49	0.47	1.13
lock'		0.75	0.36	0.00	0.79	1.91	0.25	0.00	1.23
<b>Oct-98</b>									
<i>TC</i>		0.00	6.70	13.55	5.56	1.86	4.80	11.91	2.83
<i>EB</i>		0.00	6.38	13.08	1.98	1.74	7.10	15.90	2.80
<i>St 1</i>		5.25	0.58	9.86	1.40	4.13	0.55	10.70	0.90
<i>St 2</i>		2.06	0.32	7.33	1.98	1.99	0.12	7.46	1.62
<i>St 3</i>		4.14	0.91	9.76	4.36	7.89	0.65	10.20	1.55
<i>St 4</i>		8.92	1.35	9.82	2.91	16.10	2.60	10.30	3.50
<i>ST 5</i>		16.00	3.60	11.54	4.36	14.16	5.80	20.00	6.80
TR 1		2.10	0.15	20.10	1.84	2.15	0.27	7.28	1.00
TR 2		1.97	0.27	19.99	1.89	2.15	0.15	7.33	1.76
TR 3		3.28	1.75	18.50	1.89	1.78	0.31	7.78	1.76
TR 4		2.26	0.34	19.91	1.80	2.26	0.36	8.10	1.80

n.d. = no data

\*bold, italic stations also have dome flux data for this date; see Table 3

\*lock = lock on the Trinity River north of Station 1

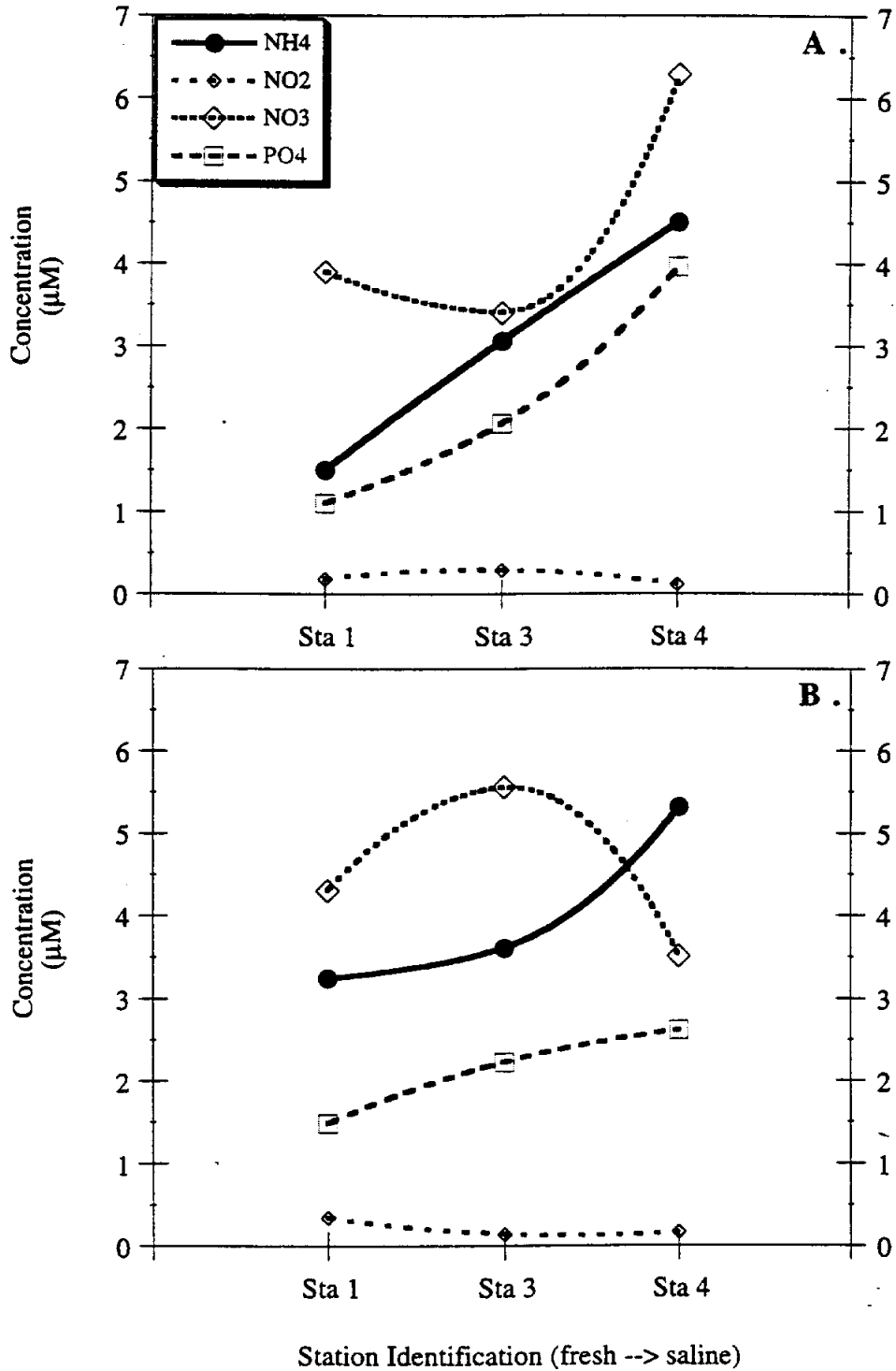
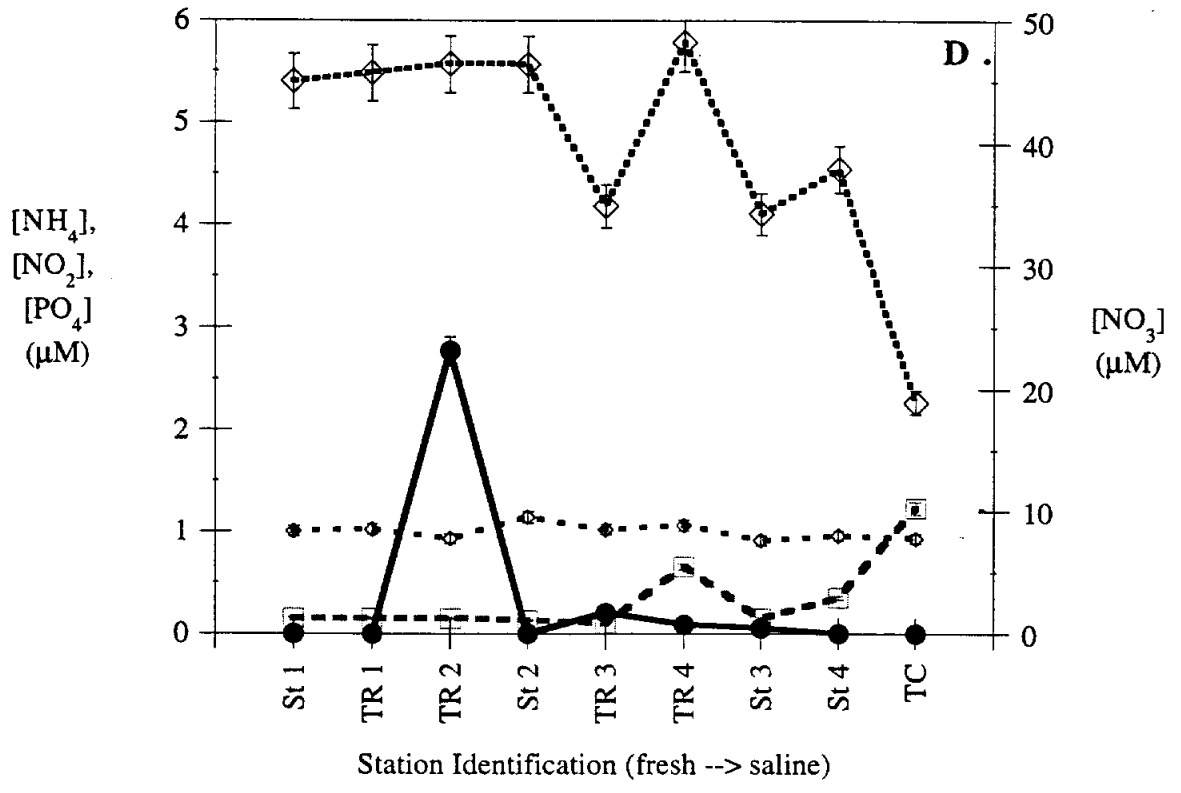
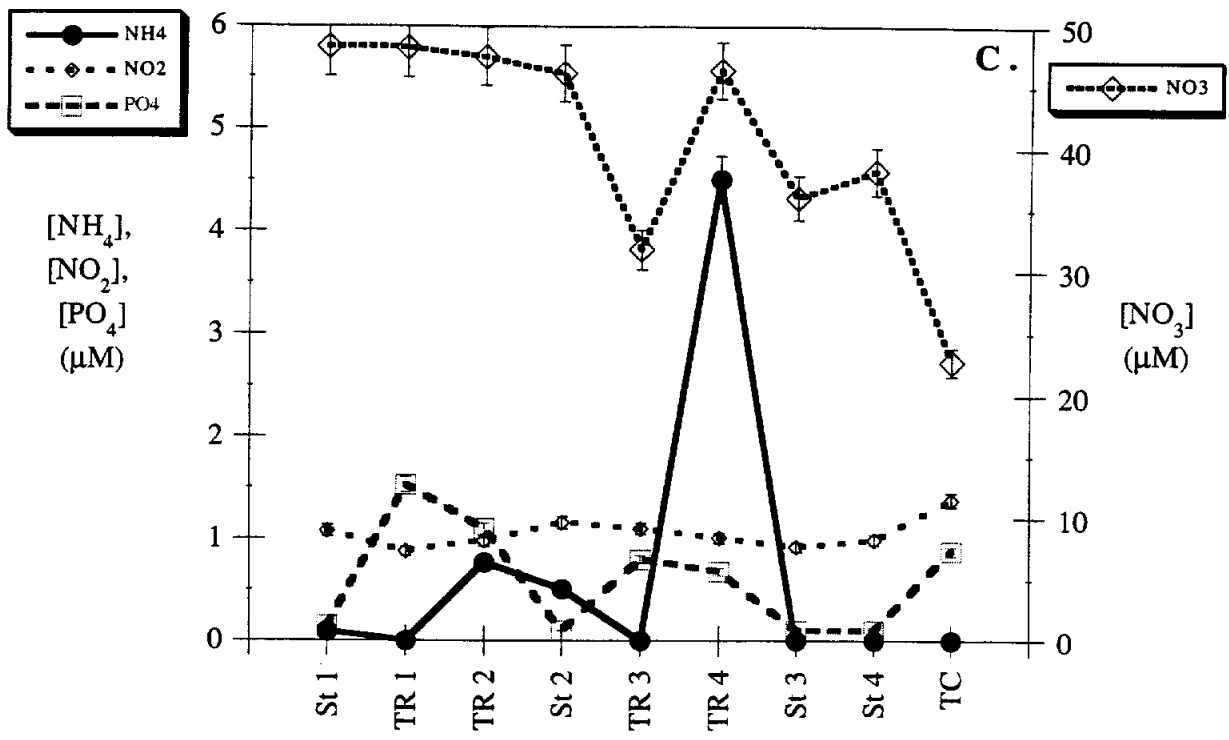
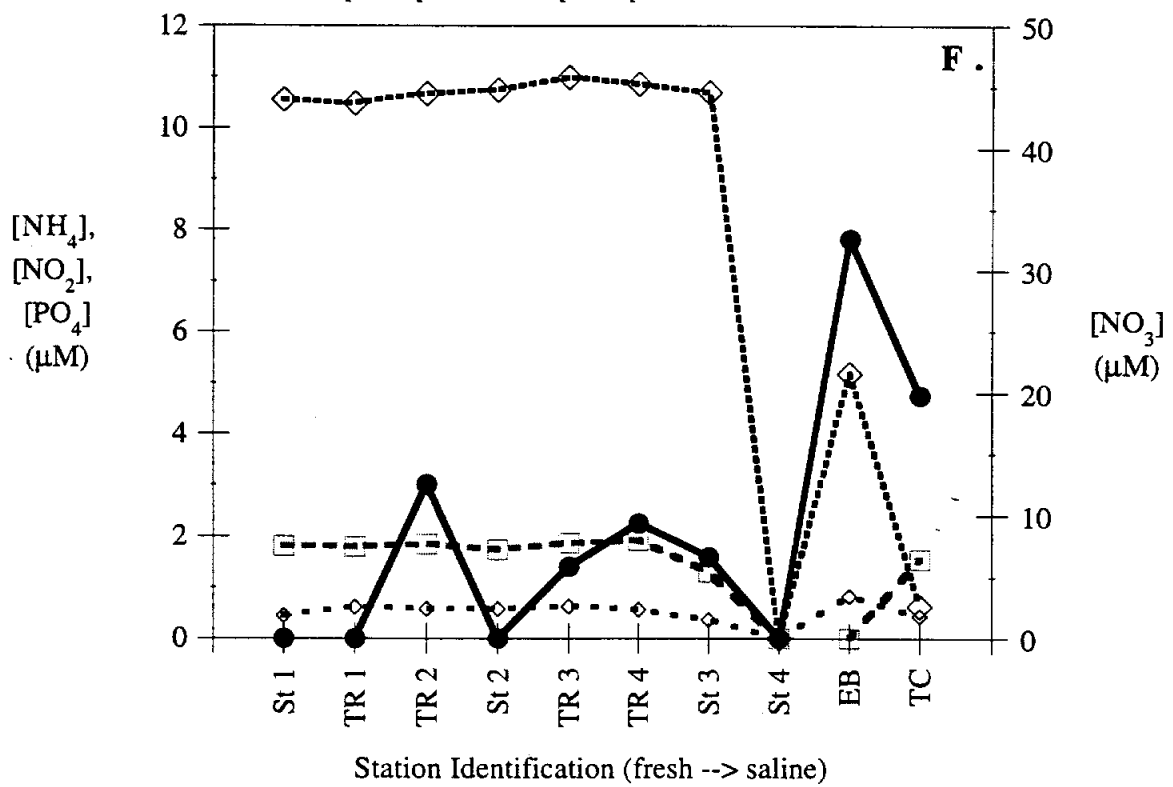
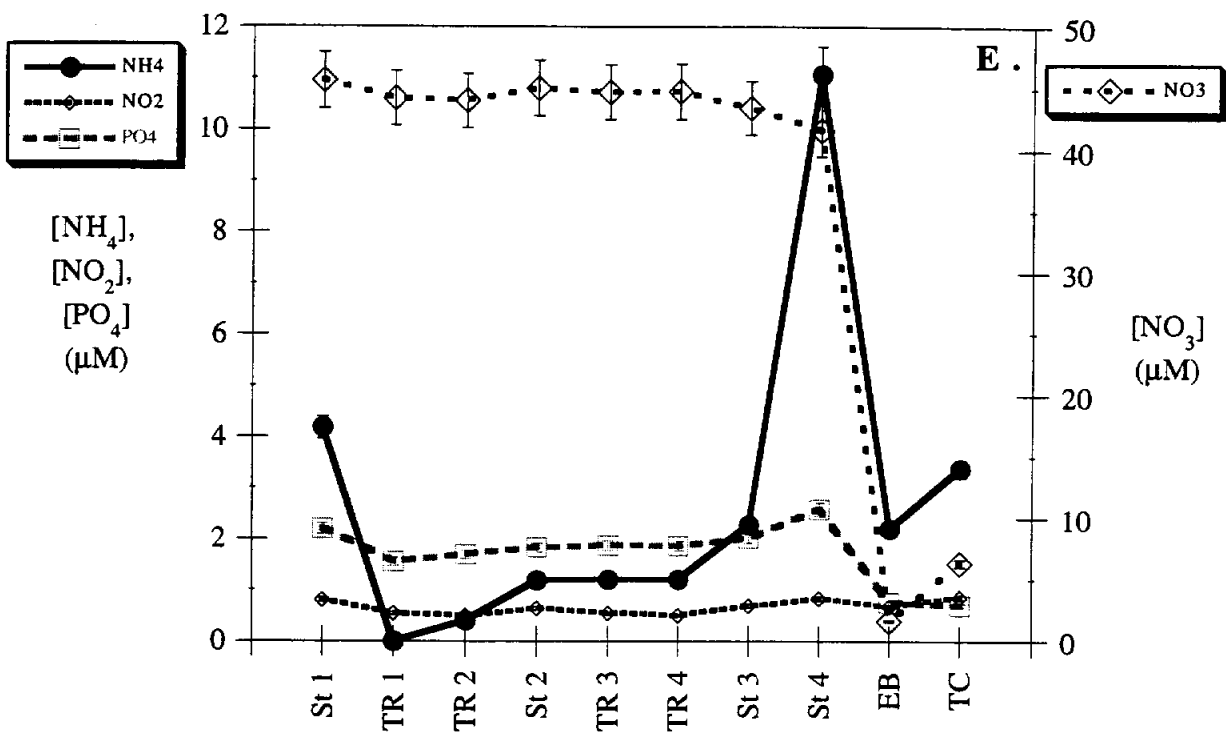
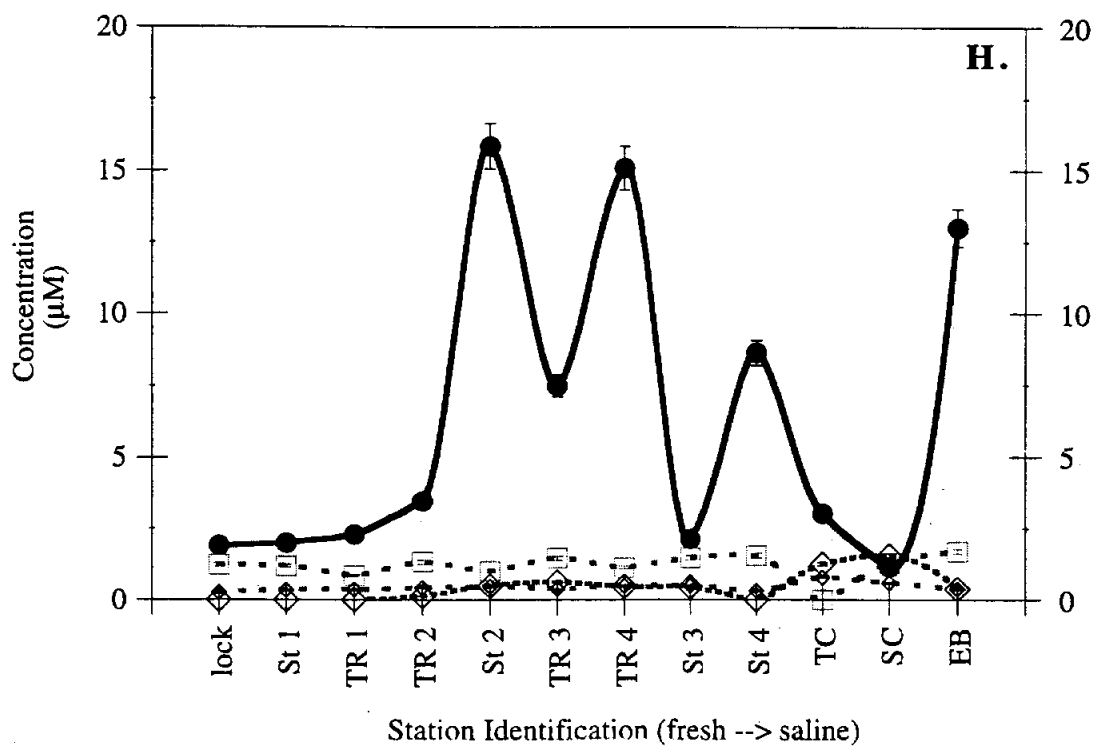
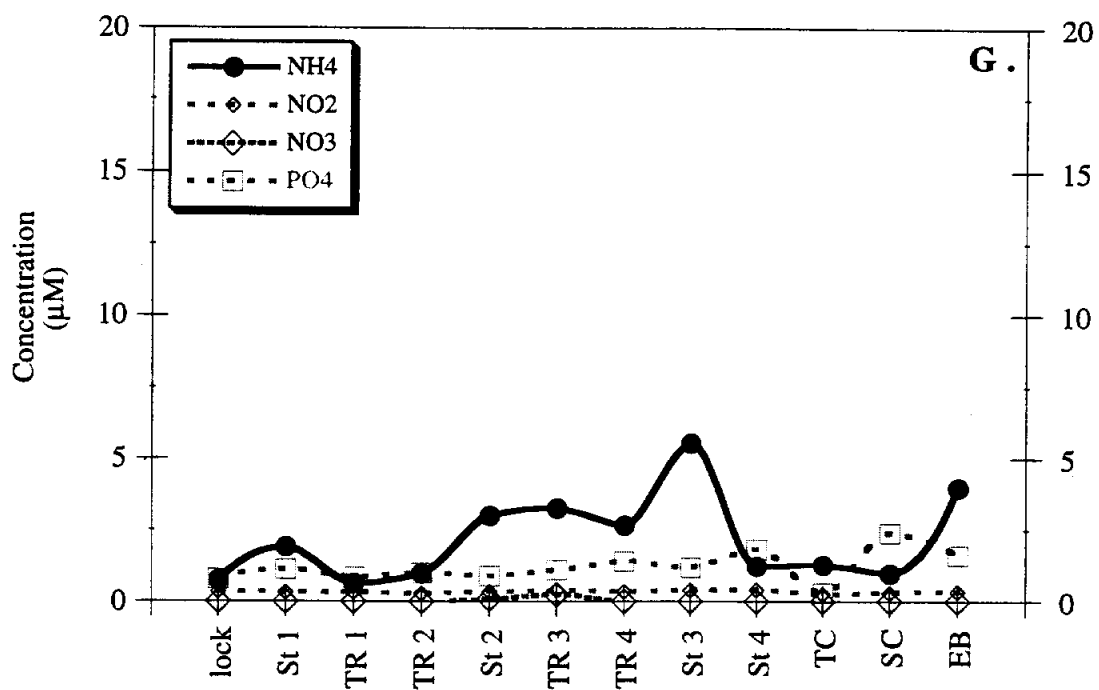
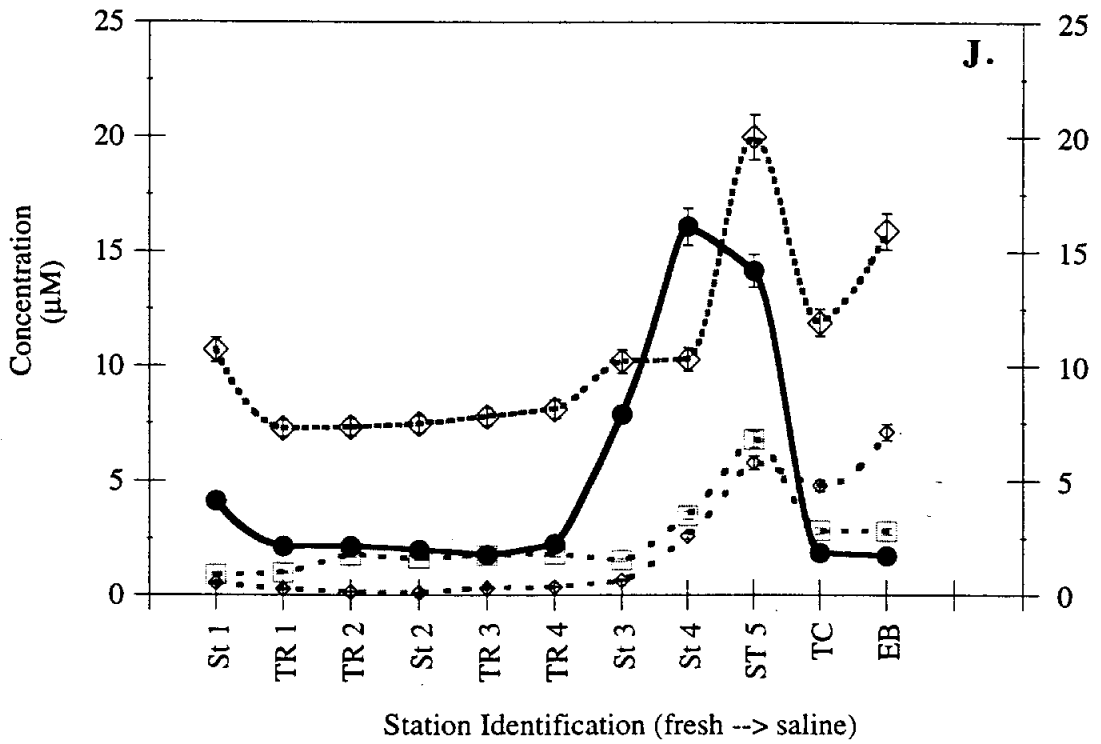
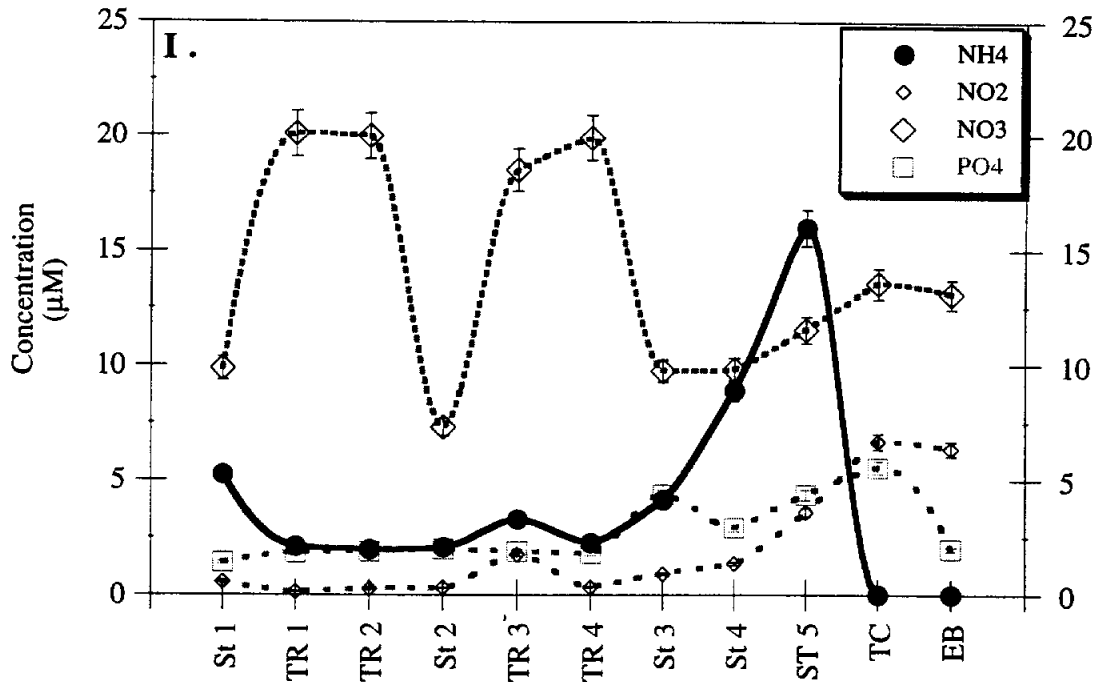


Figure 8: Surface and bottom concentration of ammonium (●), nitrite (◊), nitrate (◊), and phosphate (◻) in November 1997 (A, B); January 1998 (C, D); April 1998 (E, F); August 1998 (G, H); and November 1998 (I, J). The x-axis is station location, progressing from fresh to saline stations.











Surface water  $\text{NH}_4$  concentrations were higher during 1998 than observed during the previous years of this study (Table 2, Joye and An 1998), with maximal values ( $16 \mu\text{M}$ ) being  $\sim 4$  times higher than maximal values observed previously ( $\sim 4 \mu\text{M}$ ; Joye and An 1998). Bottom water ammonium concentrations were higher than those observed during 1997 ( $1 \mu\text{M}$ ) but similar to those observed during 1996 ( $10 \mu\text{M}$ ). Dissolved phosphate concentrations did not exhibit as much variability between 1996 and 1998. Average concentrations in surface waters were approximately  $2\text{-}3 \mu\text{M}$  during 1996 and 1998 versus  $1 \mu\text{M}$  during 1997.

Water column  $\text{NO}_3$  was the dominant inorganic N form during high flow (e.g. January 1998) whereas  $\text{NH}_4$  assumed that role during low flow (e.g. August 1998).  $\text{NO}_3$  concentrations during 1998 ( $45\text{--}50 \mu\text{M}$ ) were higher than those observed during 1996 or 1997 ( $30\text{--}35 \mu\text{M}$ ). Using data presented in Table 2, DIN (= nitrate + nitrite + ammonium) to DIP ratios  $> 45$  are obtained for the surface waters during 1998 high flow periods, suggesting the potential for P limitation of primary production. This is much higher than the DIN/DIP ratios obtained for 1996 and 1997 (DIN/DIP  $\sim 3$  to  $11$ ), which suggested N limitation of primary production. During 1998 low flow (summer) periods, DIN/DIP ratios of  $2.6$  to  $4.5$  were observed in surface waters, while DIN/DIP ratios of  $0.8\text{--}15$  (average =  $4$ ) were observed in bottom waters. The DIN/DIP ratios are well below the Redfield ratio of  $16$ , suggesting an excess of DIP compared to DIN and DIN limitation of production in Trinity Bay surface and bottom waters during summer. Similar patterns were observed at Texas City and East Bay stations during 1998, with excess DIN present during high flow (winter  $\sim$  P limitation) and excess DIP present during low flow (summer  $\sim$  N limitation).

*Pore water nutrient concentrations.* Pore water concentrations in sediment cores collected between November 1997 and October 1998 are shown in Figures 9 through 13. Pore water  $\text{NH}_4$ , nitrate + nitrite ( $\text{NO}_x$ ) and  $\text{PO}_4$  concentration exhibited significant spatio-temporal variability at all stations. Generally speaking, pore water concentrations were higher at the more saline sites and lower at the freshwater sites. In November 1997, pore water  $\text{NH}_4$  concentration ranged from 450  $\mu\text{M}$  at depth in St. 1 sediments to 1500  $\mu\text{M}$  at depth in St. 3 and 4 sediments (Fig. 9).  $\text{NO}_x$  concentration typically exhibited a sub-surface peak in concentration (ca. 5 cm), and the subsurface peak was highest at St. 4. Pore water  $\text{PO}_4$  concentrations were almost always low ( $< 2 \mu\text{M}$ ). This probably results from the binding of  $\text{PO}_4$  on to solid phase iron oxyhydroxides. In January 1998, pore water nutrient inventories at all station were much lower than those observed in Nov. 1997 (Fig. 10). At St. 3 and 4, depletion of  $\text{NH}_4$  and production of  $\text{NO}_x$  was observed throughout the upper 5 to 10 cm of the sediment column.  $\text{NO}_x$  concentrations were similar to those observed in November and exhibited either a shallow (St. 4) or deep (St. 3) sub surface peak.  $\text{PO}_4$  concentrations were higher (10  $\mu\text{M}$ ) than those observed during November and a pronounced  $\text{PO}_4$  peak was apparent at 17 cm in the St. 4 core. This peak suggests a redox change, as  $\text{NH}_4$  concentrations also begin to increase at that depth. We believe that this depth marked the depth extent of bioturbation by burrowing shrimp (An, pers. obs.). Concentrations of all pore water nutrients were extremely low at the Texas City site in January, with  $\text{NH}_4$  and  $\text{NO}_x$  concentrations being similar.

During April 1998, concentration of  $\text{NH}_4$  were similar to those observed during January, except at the Texas City site where concentrations were approximately 3-fold higher (Fig. 11).  $\text{PO}_4$  concentration was between 2-6  $\mu\text{M}$  at all sites while. Neither  $\text{NH}_4$  nor  $\text{NO}_x$  exhibited the expected depth-dependent

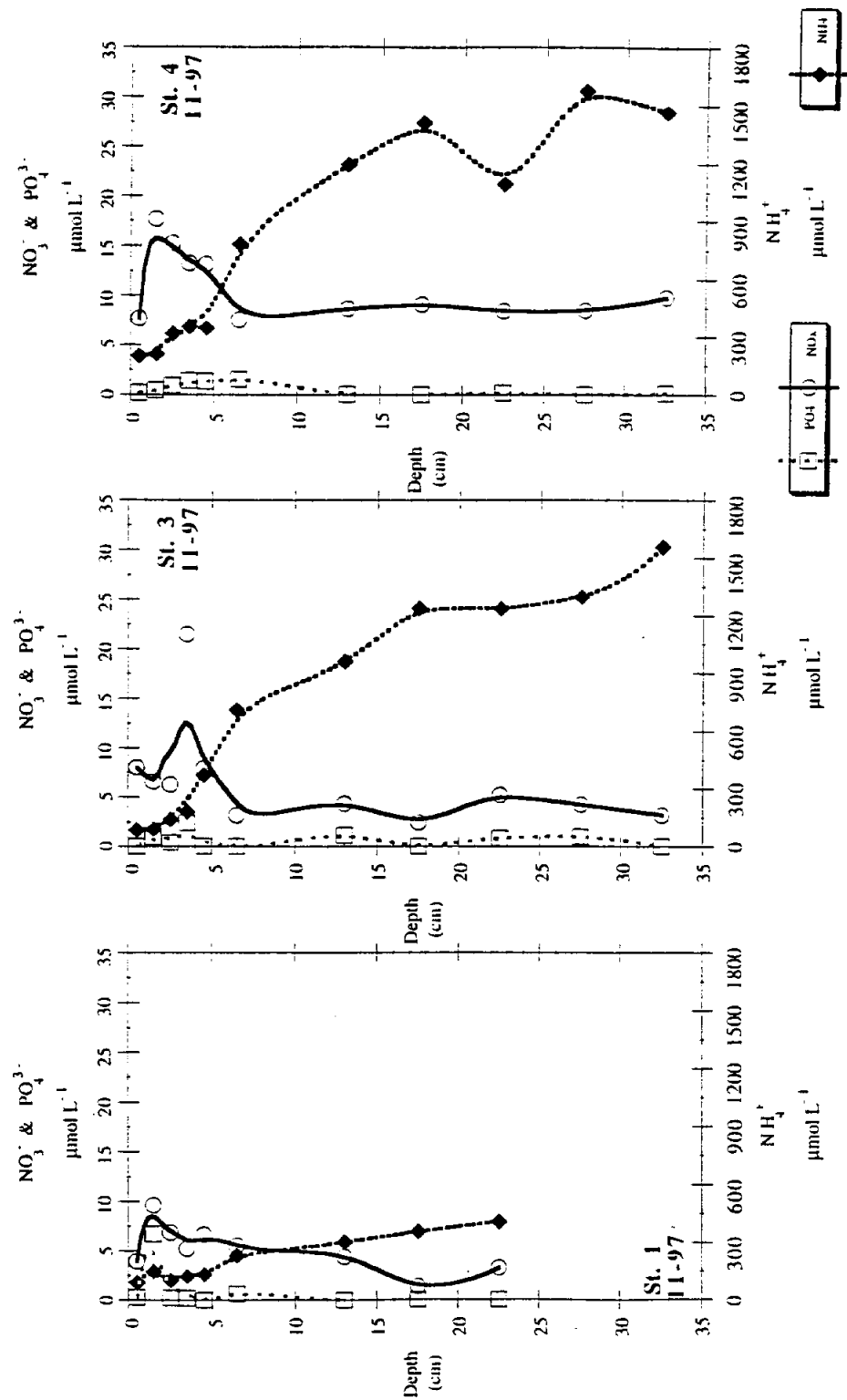


Figure 9: Pore water concentrations of ammonium ( $\blacklozenge$ ) [lower y axis] and nitrate+nitrite ( $\circ$ ) and phosphate ( $\square$ ) [upper x axis] at Sta. 1, 3 and 4 in November of 1997. Note that the scales of the two y-axes are different.

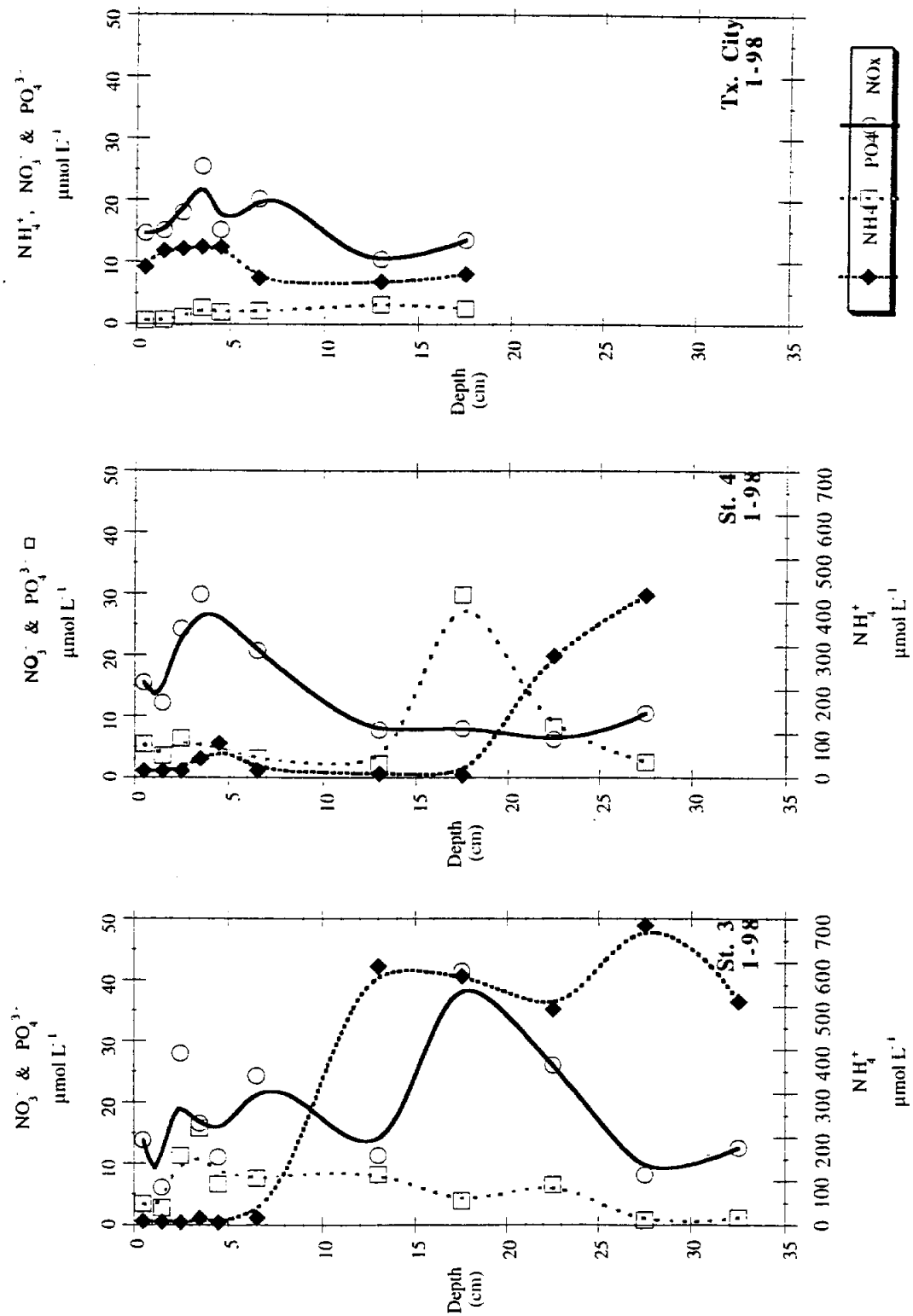


Figure 10: Pore water concentrations of ammonium ( $\blacklozenge$ ) [lower y axis] and nitrate+nitrite ( $\circ$ ) and phosphate ( $\square$ ) [upper x axis] at Sta. 3, 4 and Texas City in January of 1998. Note that the scales of the two y-axes are different.

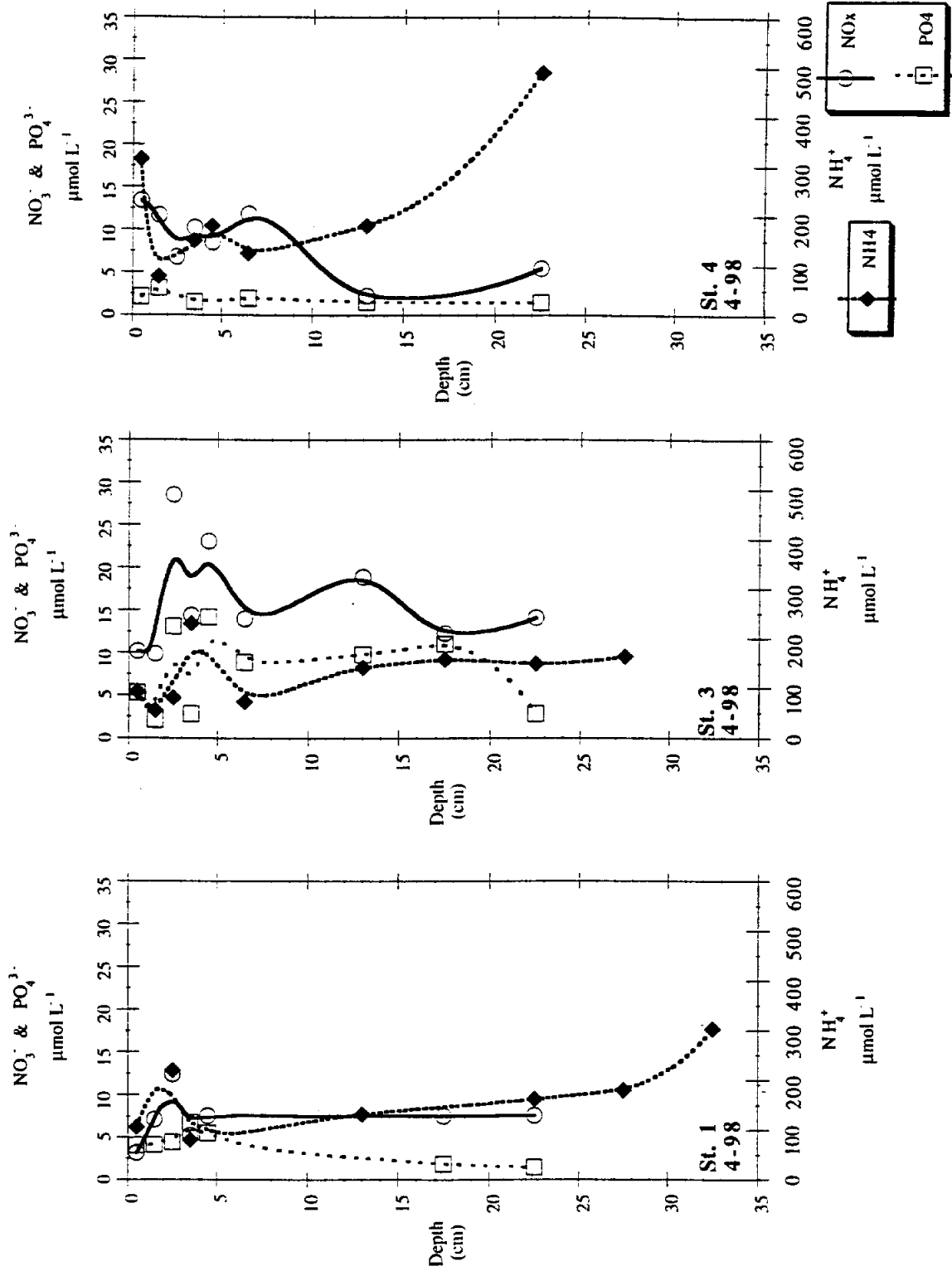
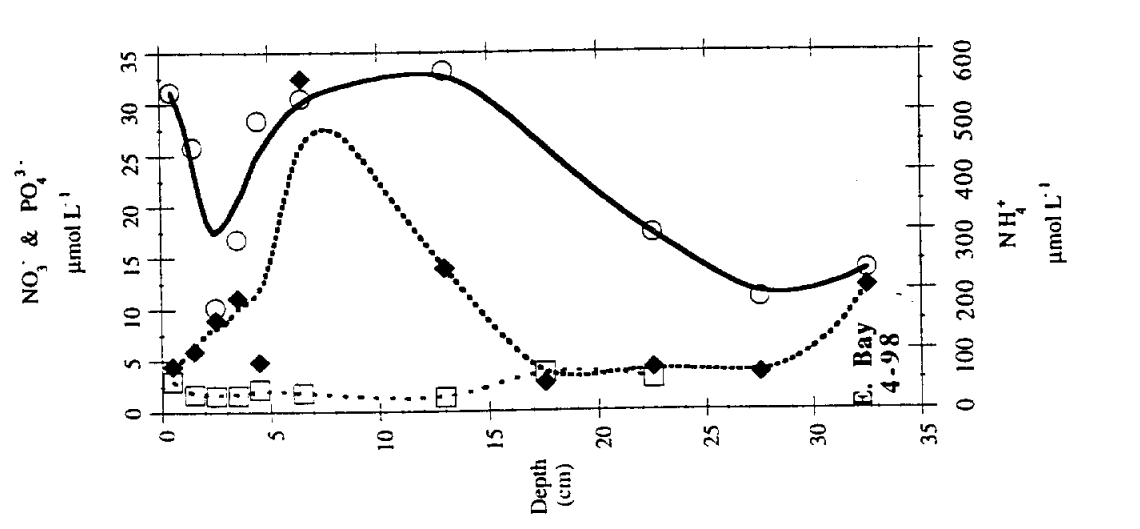
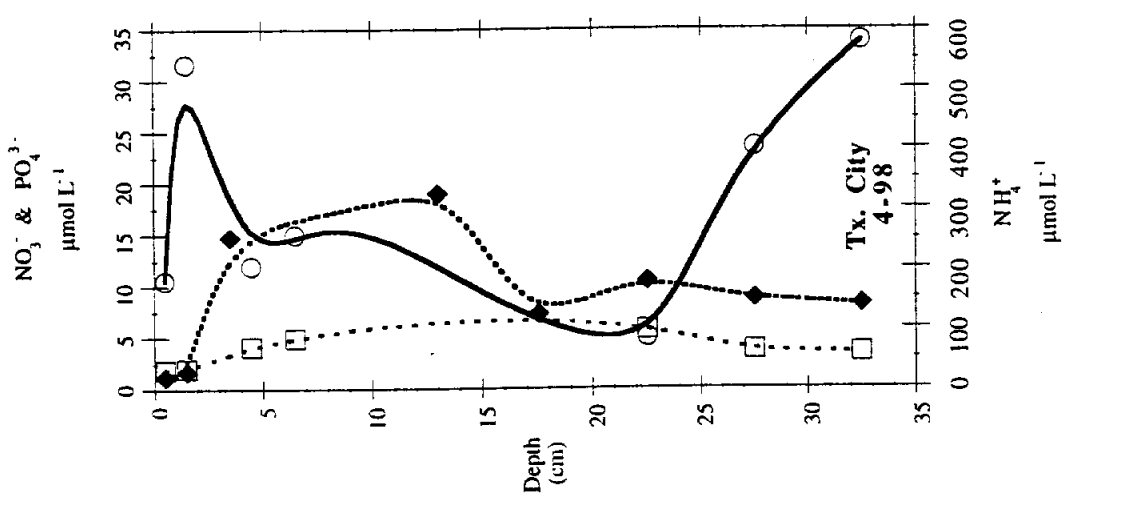
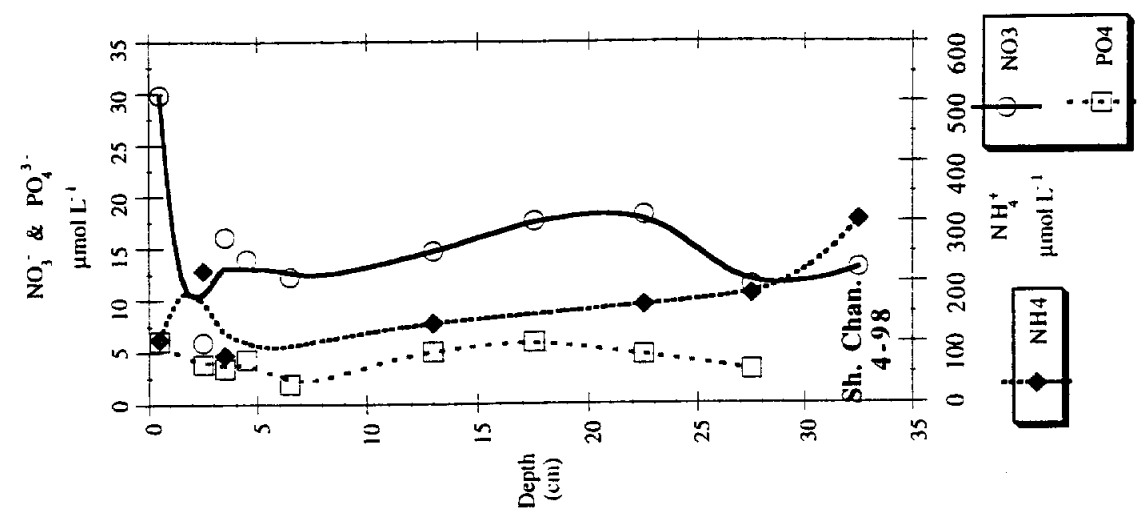


Figure 11: Pore water concentrations of ammonium (◆) [lower y axis] and nitrate+nitrite (○) and phosphate (□) [upper x axis] at Sta. 1, 3, 4, Texas City, East Bay and Ship Channel sites in April of 1998. Note that the scales of the two y-axes are different.



increase with depth. Instead, shallow (5 cm) peaks in concentration (St. 1, 3, and 4) or deep (10 cm) subsurface peaks were common at this time. In August 1998, pore water concentrations increased significantly.  $\text{NH}_4$  concentration increased with depth at the Trinity stations (St. 1, 3, 4); however, bioturbation had a significant affect on the pore water distribution of  $\text{NH}_4$  at St. 3 (Fig. 12). At the Texas City and Ship Channel stations, pore water  $\text{NO}_x$  concentrations were extremely high ( $\gg$  bottom water concentration) throughout the upper 15 cm of the sediment column.  $\text{NH}_4$  showed increased concentration with depth but concentrations were low ( $< 150 \mu\text{M}$ ; Fig. 12). Despite higher  $\text{PO}_4$  concentrations in 1998, DIN/DIP ratios were still high, probably as the result of P sorption to Fe-minerals, and the predicted DIN/DIP fluxes suggest P limitation during most of the year in the Trinity Bay region of Galveston Bay.

During November 1998, high river flow appeared to result in groundwater inputs of  $\text{NO}_x$  to pore waters. At St. 1, in particular, a deep (25 cm) peak in  $\text{NO}_x$  concentration ( $70 \mu\text{M}$ ) was observed. We believe this deep peak reflects groundwater input to river sediments. At St. 3 and 4, the depth distribution patterns of  $\text{NO}_x$  and  $\text{NH}_4$  were similar. As we have seen before, bioturbation results in erratic changes in pore water nutrient concentrations. At St. 5,  $\text{NH}_4$  concentrations increase linearly with depth and  $\text{PO}_4$  concentrations also increase. These are the highest  $\text{PO}_4$  concentrations ever measured in Galveston Bay pore water (by us). The absence of  $\text{NO}_x$  at depth and the clear pattern of  $\text{NH}_4$  and  $\text{PO}_4$  increase suggest that St. 5 sediments differ from sediments at St. 3 and 4, in that they are not well mixed (bioturbated) and in fact, they are probably anoxic/sulfidic at depths greater than 20 cm (Fig. 13).

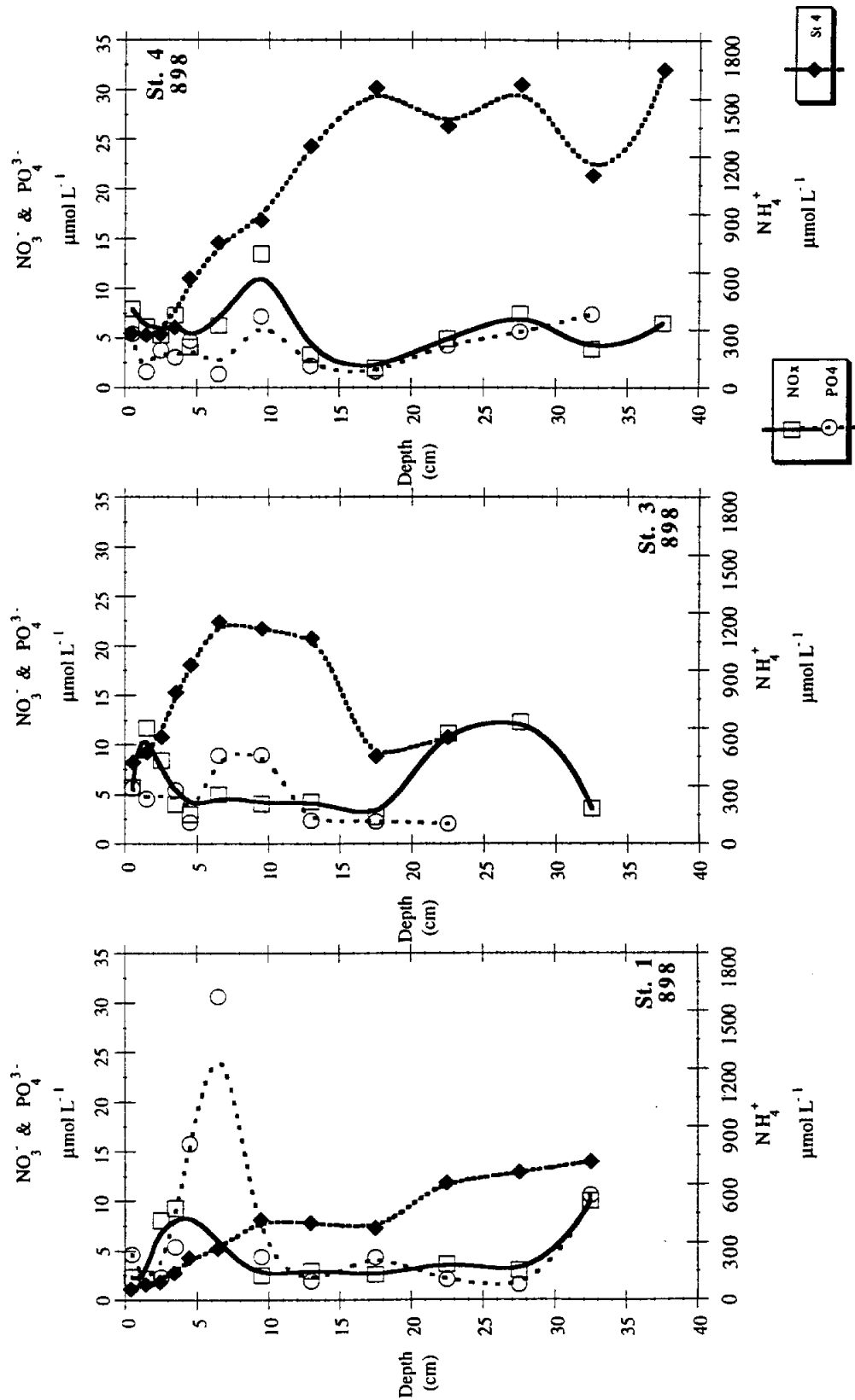
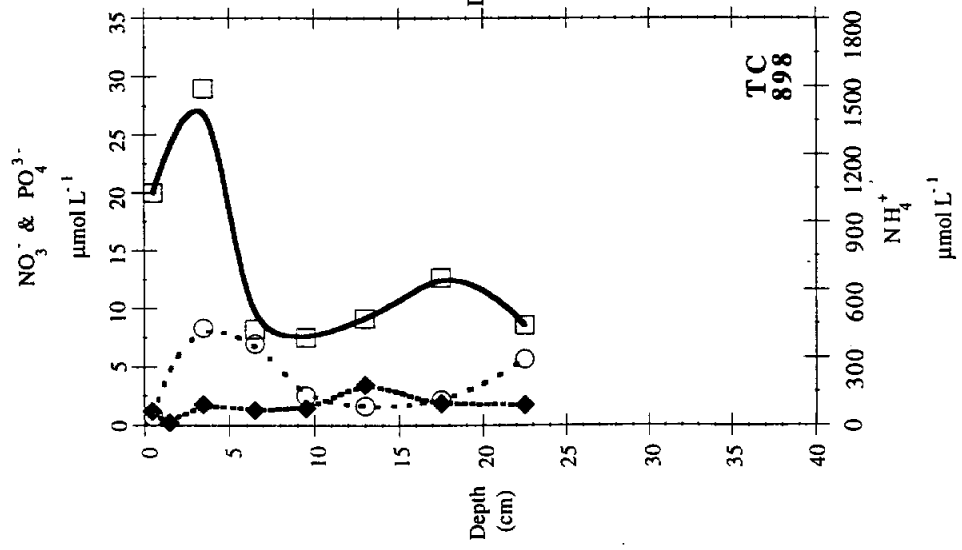
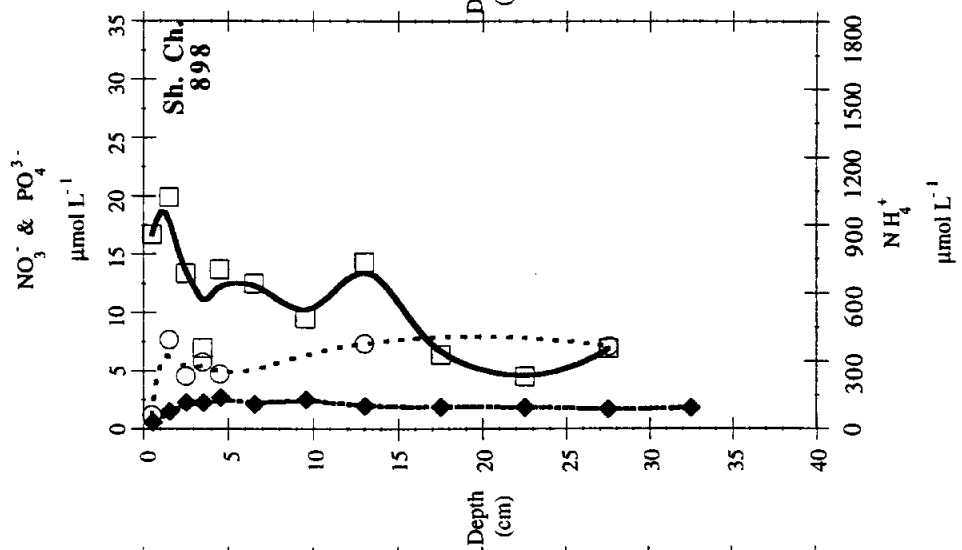
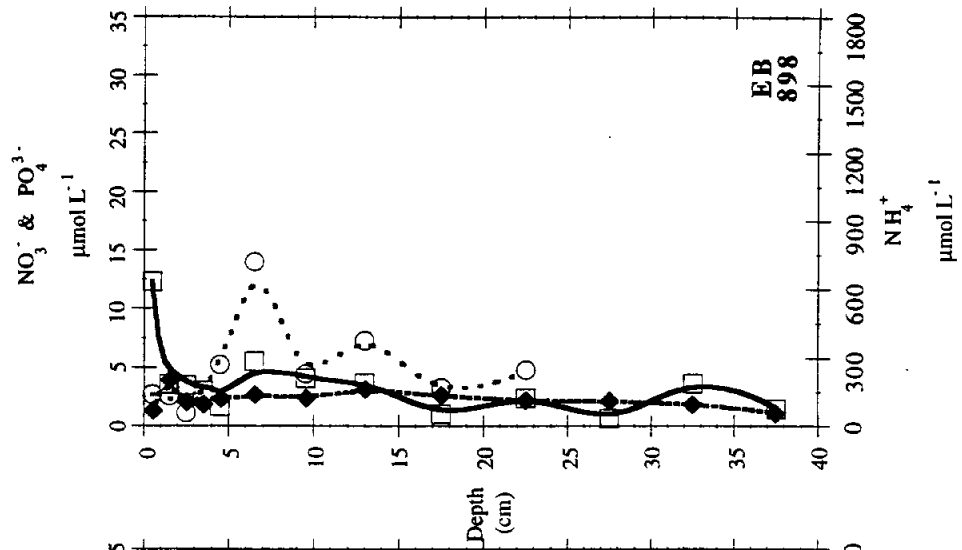


Figure 12: Pore water concentrations of ammonium ( $\blacklozenge$ ) [lower y axis] and nitrate+nitrite ( $\circ$ ) and phosphate ( $\square$ ) [upper x axis] at Sta. 1, 3, 4, Texas City, East Bay and Ship Channel sites in August of 1998. Note that the scales of the two y-axes are different.





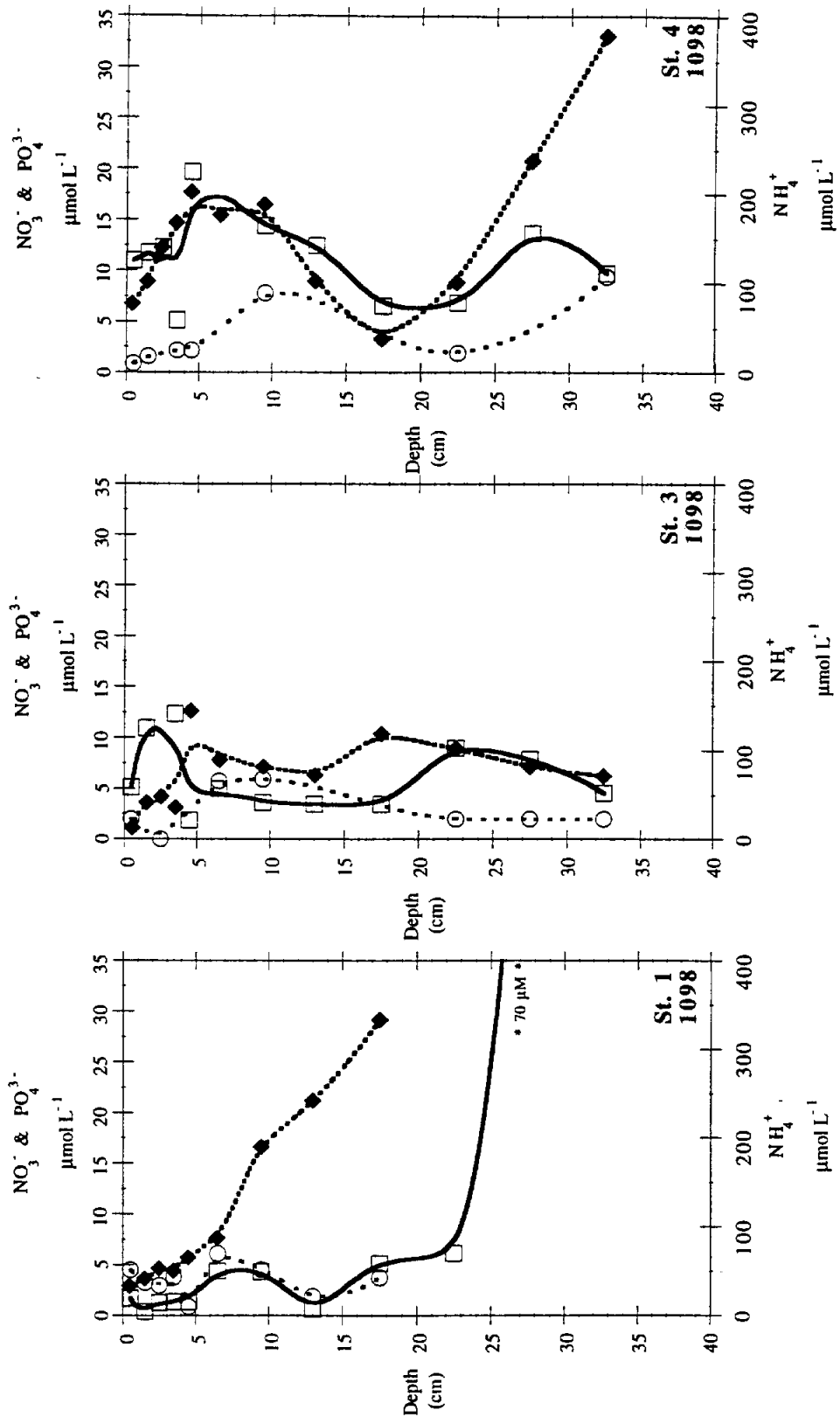
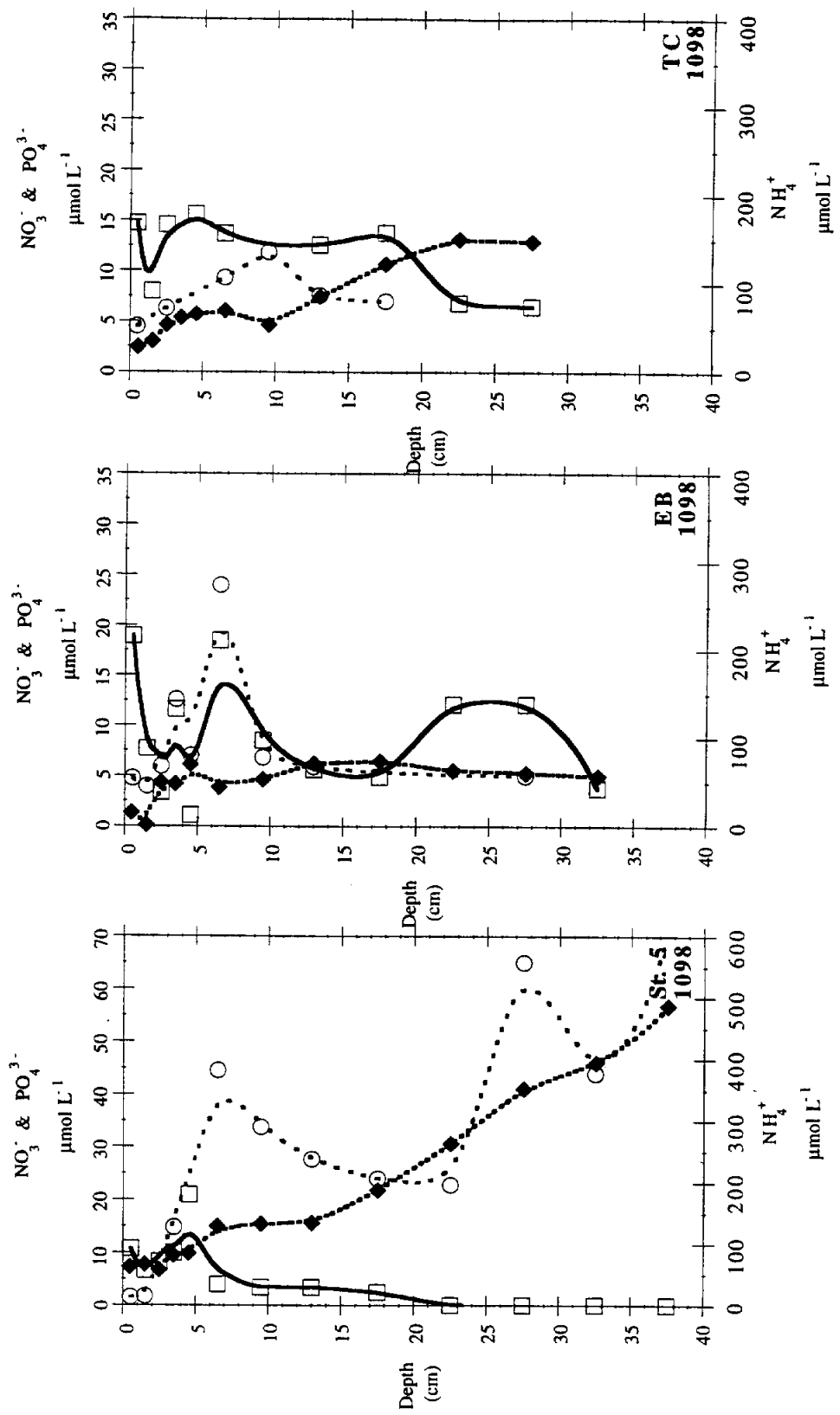


Figure 13: Pore water concentrations of ammonium ( $\blacklozenge$ ) [lower y axis] and nitrate+nitrite ( $\circ$ ) and phosphate ( $\square$ ) [upper x axis] at Sta. 1, 3, 4, 5, Texas City and East Bay sites in November of 1998. Note that the scales of the two y-axes are different.



*Benthic fluxes.* A significant fraction of terrestrial nitrogen input to estuaries is lost via denitrification (Seitzinger 1988; Nixon et al. 1996; Nowicki et al. 1997). When denitrification is a major loss term, the process will either mitigate the impact of increased nitrogen loading or result in nitrogen limitation of ecosystem production (Seitzinger 1988; Nishio et al. 1982; Nixon et al. 1996; Seitzinger 1990). Studies of denitrification including the seasonal pattern, the controlling factors and the importance of the process as a nitrogen removal process is necessary to assess the impact of modified nitrogen loading either by natural or anthropogenic perturbations (Brock et al. 1996).

Benthic primary production transforms regenerated inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_x$ ) into organic forms at the sediment water interface (An 1999). The aerobic microenvironment created by benthic primary producers, however, is more important to nitrogen cycling than the organic matter production itself (Revsbech et al. 1988). For example when sediment nitrification and denitrification coupling is dependent on  $\text{O}_2$  availability (Kemp et al. 1990), increased oxygen availability resulting from benthic primary production can – indirectly - enhance denitrification (Risgaard-Petersen et al. 1994; Tomaszek et al. 1997). Benthic primary production in shallow estuaries is primarily light limited (Revsbech et al. 1988; MacIntyre and Cullen 1996). In many shallow estuaries, however, benthic microalgae can be significant primary producers (Pinckney and Zingmark 1991). Furthermore, their influence on benthic processes such as aerobic respiration, nitrification, and denitrification (Revsbech et al. 1988; Tomaszek et al. 1997; Boudreau 1997) can be significant. In the case of nitrogen cycling in a shallow estuary like Galveston Bay, the role of benthic primary production must be considered.

A large portion of our effort in this study has focused on determining the nature of freshwater and nutrient inputs to Galveston Bay and then on correlating biogeochemical activity with those variables (originally discussed in Joye and An 1998). To evaluate the importance of benthic primary production in Galveston Bay, parameters relating to light availability (freshwater discharge, water column chlorophyll and Secchi depth) were determined (Joye and An 1998; An 1999). The seasonal patterns of benthic processes that impact nitrogen transformations, such as remineralization, nitrification and denitrification, were related to various environmental conditions that might affect the processes. Finally, the importance of denitrification as a nitrogen sink in Galveston Bay was determined.

*Freshwater inflow.* Freshwater inflow was estimated from gauged data gathered at USGS station # 8066500 which is located along the Trinity River at Romayor. The amount of freshwater gauged at this station probably accounts for 94% of estimated total freshwater input to Trinity Bay and 45% of the inflow to the entire estuary from the drainage basin. Whole bay average fresh water input was obtained from Brock et al. (1996). A very good linear relationship exists between the gauged data and freshwater input averaged during 1988-1990 (Brock et al. 1996). The average freshwater input to Galveston Bay is  $907 \times 10^6 \text{ m}^3 \text{ month}^{-1}$ . The freshet (high amount of freshwater input) usually occurs during winter and spring. The average input at this time is  $1370 \times 10^6 \text{ m}^3 \text{ month}^{-1}$  (An 1999). During summer and fall, there is a dramatic decrease of freshwater input ( $140\text{-}580 \times 10^6 \text{ m}^3 \text{ month}^{-1}$ ). In the first year of our study, 1996, the freshwater input was averaged  $179 \times 10^6 \text{ m}^3 \text{ month}^{-1}$ . Hydraulic residence time (t), estimated from the freshness (f), the volume of the bay (V) and the freshwater inflow (Q;  $t = f \cdot V / Q$ ;

Armstrong 1982), varied from a month (33 days) during high flow to 8 months during low flow (summer and fall).

The total nitrogen input into Galveston Bay (gauged stream flow + ungauged rainfall runoff + waste water returns + direct rainfalls) between 1988 to 1990 was estimated by Brock et al. (1996). A good relationship was observed between total N loading and freshwater discharge (Joye and An 1998; An 1999). A linear equation was obtained using data from 1988-1990 ( $\text{N loading (10}^6 \text{ mole N)} = 2.7689 \times \text{freshwater discharge (10}^6 \text{ m}^3 \text{ month}^{-1}) + 749.99$  ( $R^2 = 0.99$ ; Joye and An 1998; An 1999). The total N loading to the bay between 1994-1998, calculated using this equation, averaged  $168 \times 10^6 \text{ mol N month}^{-1}$ .

In Galveston Bay, benthic primary production is an important variable that influences various benthic processes (An 1999). For example, at Station 3 where the benthic primary production is high (see below), measured  $\text{NH}_4$  uptake by sediments contradicted the calculated flux based on pore water profiles (An 1999). Benthic primary producers probably consume  $\text{NH}_4$  during photosynthesis. The activity of benthic microalgae should be highest at the surface of the sediment interface and the algae may intercept the nutrient flux (An 1999).

In our 1998 report, we showed that chlorophyll *a* concentrations in surface sediments were extremely high, up to  $1000 \text{ mg m}^{-2}$  (Joye and An 1998; An 1999). Chlorophyll *a* concentration was low at the freshwater stations (1 and 2) of the Trinity River. The average benthic chlorophyll concentration was  $500 \text{ mg chl. } a \text{ m}^{-2}$  (An 1999). While these chlorophyll concentrations are lower than those typical of benthic microalgal mats ( $10^3 - 10^6 \text{ mg chl. } a \text{ m}^{-2}$ ), they are similar to

those observed in other coastal environments (Krause-Jensen and Sand-Jensen 1998; Joye et al. 1996) and infer the importance of benthic primary production.

Warnken (1998) documented  $19 - 65 \text{ mmole O}_2 \text{ m}^{-2} \text{ d}^{-1}$  of benthic primary production in Trinity Bay (near our St. 3 & 4) during March 1996 using a light-dark chamber technique. In this current study, we documented  $16 \text{ mmole O}_2 \text{ m}^{-2} \text{ d}^{-1}$  net photosynthesis (photosynthesis - total sediment oxygen demand; see discussion below) at Station 3 in November 1997. The measured benthic primary production rate in Galveston Bay is higher than the rates found in shallow subtidal sediments of North inlet, South Carolina ( $12 \text{ mmole O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ; Pinckney and Zingmark 1993). However, the measurements of benthic primary production made during this study are not enough to delineate the range of benthic primary production rates in Galveston Bay. Despite this, the measured rates are comparable to values obtained for water column primary production in Galveston Bay ( $50\text{-}500 \text{ mmole O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , see below).

*Seasonal and spatial variation of denitrification.* The average denitrification rate estimated for Galveston Bay sediments during this study was  $1.80 \text{ mmole N}_2 \text{ m}^{-2} \text{ d}^{-1}$  (Table 3). The highest rate,  $4.58 \text{ mmole m}^{-2} \text{ d}^{-1}$ , was measured in Nov. 1997 at Station 1 (Table 4). During summer, rates were high as was variability between sites ( $1.93 \text{ mmole m}^{-2} \text{ d}^{-1}$  at Texas City to  $4.32 \text{ mmole m}^{-2} \text{ day}^{-1}$  at Station 5; Table 3, Figure 14). Denitrification rates were low during winter, except in Jan-98 at Station 4, when the rate was comparable to the spring and autumn values measured at the same station. Interannual variability was high at Station 4 ( $0.60$  and  $1.47 \text{ mmole m}^{-2} \text{ day}^{-1}$  in Jan. 1997 and 1998, respectively) and low in Texas City ( $0.58$  and  $0.78 \text{ mmole m}^{-2} \text{ day}^{-1}$  in Jan. 1997 and 1998, respectively) (Table 3-1). In Aug. 1997, the denitrification rates in two new

Table 3. Benthic fluxes of inorganic nitrogen,  $N_2$ ,  $O_2$  and dissolved inorganic carbon ( $mmole\ m^{-2}d^{-1}$ ) in Galveston Bay. Positive values represent the fluxes out of sediment. Grain size (% sand) and salinity (ppt), temperature ( $^{\circ}C$ ),  $NO_3$  and  $NH_4$  concentration of bottom water are also presented. *ND* : no data.

Month	Station	sand (%)	salinity (ppt)	Temp. ( $^{\circ}C$ )	[ $NO_3$ ] ( $\mu M$ )	[ $NH_4$ ] ( $\mu M$ )	$N_2$	$NO_3$ + $NO_2$	$NH_4$	$O_2$	DIC
Jun-96	ST4	14	15	27	<i>ND</i>	<i>ND</i>	1.67	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
Aug-96	ST2	98	1.5	30	2.7	14.0	2.04	-0.25	2.97	-2.04	<i>ND</i>
	ST3	17	12		2.1	14.0	1.31	-0.17	-1.83	-18.97	<i>ND</i>
	Texas City	87	17		0.8	0.0	1.04	0.04	0.28	-10.39	<i>ND</i>
Oct-96	ST4	90	3.5	24.5	8.0	12.3	0.90	-0.09	0.64	-14.32	18.45
	Texas City	81	15		5.4	3.7	2.57	-0.01	-0.55	-2.00	3.00
Jan-97	ST4	21	5	15.4	0.7	0.3	0.60	0.01	0.03	-2.00	1.15
	Texas City	78	23		0.5	0.0	0.58	-0.01	0.00	-1.80	4.50
Apr-97	ST1	99	0	19.8	34.3	1.9	<i>ND</i>	2.60	-0.19	<i>ND</i>	30.39
	ST4	55	0		37.6	1.0	1.03	-1.12	-0.05	-7.06	36.60
	Texas City	79	1.2		16.3	0.5	0.69	0.02	-0.05	-7.28	9.60
Jul-97	ST2	98	0	31.2	1.0	<i>ND</i>	2.30	-0.02	0.10	-6.31	29.20
	ST3	17	0		1.7	0.4	2.04	-0.13	0.14	-4.53	40.53
	ST4	76	0.4		0.1	0.9	2.45	0.27	0.11	-8.54	21.39
	Texas City	88	23.8		0.2	0.8	1.87	0.02	0.94	-6.62	18.35
Aug-97	ST3	17	3.4	31	0.9	1.3	<i>ND</i>	0.00	0.49	7.40	12.09
	ST4	<i>ND</i>	5.3		0.9	0.2	2.26	0.14	0.43	-9.41	31.36
	ST5	49	7.8		0.8	0.0	4.32	0.95	1.05	-11.12	32.80
	East Bay	14	12.5		1.0	2.9	2.80	-0.02	1.36	-8.50	25.40
	Texas City	86	28.6		0.4	0.6	1.93	0.02	0.82	-9.23	18.76
Nov-97	ST1	99	0	15.6	4.2	4.6	4.58	-0.48	2.25	-5.49	36.30
	ST3	17	0.4		4.2	4.2	3.94	-0.14	-0.12	15.90	5.62
	ST4	<i>ND</i>	0.4		3.6	5.5	1.79	0.13	1.58	-9.11	19.31
Jan-98	ST3	17	0	14.5	36.4	3.0	0.29	-0.64	-0.12	1.70	9.85
	ST4	<i>ND</i>	0		39.1	<i>ND</i>	1.47	-0.64	<i>ND</i>	-9.30	<i>ND</i>
	Texas City	83	13		20.5	<i>ND</i>	0.78	-1.95	<i>ND</i>	-1.03	11.68
Apr-98	ST1	<i>ND</i>	0	18	44.0	0.0	1.40	-0.83	0.85	-1.39	<i>ND</i>
	ST3	<i>ND</i>	0		44.6	0.0	2.62	-2.10	1.30	16.83	<i>ND</i>
	ST4	<i>ND</i>	0		41.0	0.0	2.79	<i>ND</i>	<i>ND</i>	0.97	<i>ND</i>
	East Bay	<i>ND</i>	2		21.6	7.8	1.06	0.06	-0.36	1.61	<i>ND</i>
	Texas City	<i>ND</i>	2.5		2.6	4.8	0.44	-0.06	1.55	1.55	<i>ND</i>
	Ship Chan.	<i>ND</i>	5		<i>ND</i>	3.2	1.43	0.07	2.58	-3.95	<i>ND</i>
Aug-98	East Bay	<i>ND</i>	20.4	31	0.4	13.0	0.99	0.00	1.99	-10.16	<i>ND</i>
	Texas City	<i>ND</i>	31.3		0.8	3.0	1.05	0.01	1.69	-6.68	<i>ND</i>
	Ship Chan.	<i>ND</i>	31		0.6	1.2	1.94	0.01	1.90	-6.99	<i>ND</i>
Oct-98	ST1	<i>ND</i>	0	20	10.7	4.1	2.23	-0.23	-0.08	-2.26	<i>ND</i>
	ST3	<i>ND</i>	0		10.2	7.9	0.11	-0.16	0.89	-6.20	<i>ND</i>
	ST4	<i>ND</i>	5.8		10.3	16.1	3.42	-0.18	1.42	-4.71	<i>ND</i>
	ST5	<i>ND</i>	6.4		20.0	14.2	1.37	0.08	0.41	-3.00	<i>ND</i>
	East Bay	<i>ND</i>	11.4		15.9	1.7	0.84	-0.66	0.45	-4.27	<i>ND</i>
	Texas City	<i>ND</i>	19.5		11.9	1.8	0.47	0.25	0.28	-2.65	<i>ND</i>

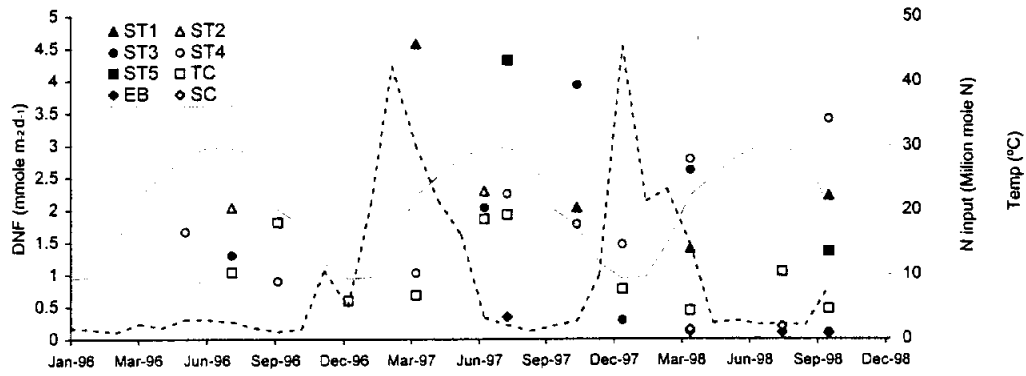


Table 4. Percent of denitrification supported by water column  $\text{NO}_3+\text{NO}_2$  influx, nitrification,  $\text{O}_2$  demand by nitrification, N efflux and respiratory quotient for Galveston Bay sediment. The calculations are based on the data in Table 3. ND: no data.

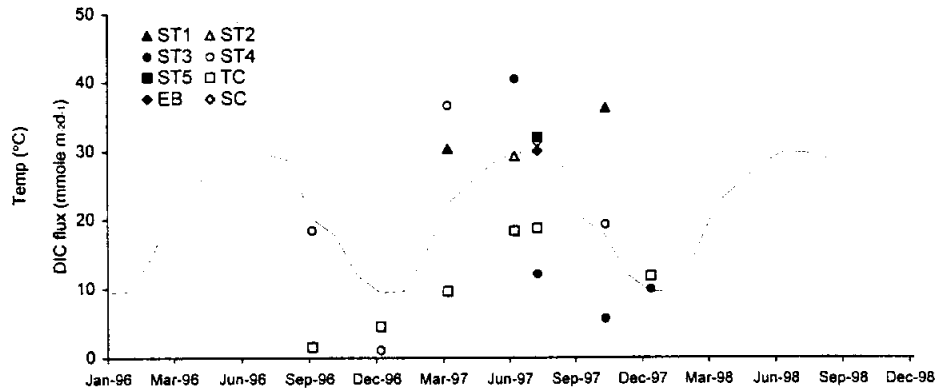
Month	Station	$\text{N}_2$ Production supported by $\text{NO}_3+\text{NO}_2$ influx* (%)	Nitrification <sup>b</sup> ( $\text{mmole m}^{-2} \text{d}^{-1}$ )	$\text{O}_2$ needed for Nitrification <sup>c</sup> ( $\text{mmole m}^{-2} \text{d}^{-1}$ )	% of SOD	N efflux <sup>d</sup> ( $\text{mmole m}^{-2} \text{d}^{-1}$ )	% benthic N efflux that is $\text{N}_2$ <sup>e</sup>	R.Q. <sup>f</sup>
Aug-96	ST2	6.1	3.83	7.7	375	5.01	40.7	ND
	ST3	6.6	2.45	4.9	26	1.31	100.0	ND
	Texas City		2.12	4.2	41	1.36	76.6	ND
Oct-96	ST4	5.1	1.71	3.4	24	1.54	58.6	1.3
	Texas City	0.2	3.62	7.2	924	1.81	100.0	2.0
Jan-97	ST4	ND	1.21	2.4	121	0.64	94.1	0.6
	Texas City	0.9	1.15	2.3	128	0.58	100.0	2.5
Apr-97	ST4	54.5	0.94	1.9	27	1.03	100.0	5.2
	Texas City		1.40	2.8	38	0.71	97.9	1.3
Jul-97	ST2	0.4	ND	ND	ND	2.30	100.0	4.6
	ST3	3.3	3.95	7.9	174	2.18	93.4	8.9
	ST4	ND	5.17	10.3	121	2.83	86.6	2.5
	Texas City	ND	3.75	7.5	113	2.83	66.0	2.8
Aug-97	ST4	ND	4.66	9.3	99	2.83	79.9	3.3
	ST5	ND	9.58	19.2	172	6.32	68.3	3.0
	East Bay	0.4	5.58	11.2	131	4.16	70.3	3.3
	Texas City	0.0	3.89	7.8	84	2.78	67.3	2.0
Nov-97	ST1	5.2	8.68	17.4	316	6.83	67.0	6.6
	ST3	1.8	7.74	15.5	-97	3.94	100.0	ND
	ST4	ND	3.70	7.4	81	3.49	51.2	2.1
Jan-98	ST3	109.8	0.00	0.0	0	0.29	100.0	ND
	ST4	ND	2.30	4.6	49	1.47	100.0	ND
	Texas City	125.8	0.00	0.0	0	0.78	100.0	11.3
Apr-98	ST1	59.3	0.37	0.7	53	2.25	62.2	ND
	ST3	80.2	0.52	1.0	75	3.92	33.2	ND
	ST4	ND	ND	ND	ND	ND	ND	ND
	East Bay	0.0	1.06	2.1	+SOD	1.12	94.6	ND
	Texas City	13.6	0.14	0.3	+SOD	1.99	22.1	ND
	Ship Chan.	0.0	1.43	2.9	72	4.08	35.0	ND
Aug-98	East Bay	0.0	0.99	2.0	19	2.98	33.2	ND
	Texas City	0.0	1.05	2.1	31	2.75	38.5	ND
	Ship Chan.	0.0	1.94	3.9	56	3.85	50.4	ND
Oct-98	ST1	10.3	2.00	4.0	177	2.23	100.0	ND
	ST3	145.5	0.00	0.0	0	1.00	11.0	ND
	ST4	5.3	3.24	6.5	138	4.84	70.7	ND
	ST5	0.0	1.37	2.7	91	1.86	73.7	ND
	East Bay	78.6	0.18	0.4	8	1.29	65.1	ND
	Texas City	0.0	0.47	0.9	35	1.00	47.0	ND
<b>Average</b>		<b>25.5</b>	<b>2.6</b>	<b>5.1</b>	<b>109</b>	<b>2.5</b>	<b>71.7</b>	<b>3.7</b>
<b>Std dev</b>		<b>43.2</b>	<b>2.4</b>	<b>4.9</b>	<b>169</b>	<b>1.6</b>	<b>26.3</b>	<b>2.9</b>

a:  $(\text{NO}_3+\text{NO}_2 \text{ flux})/(\text{N}_2 \text{ flux} \times 2) \times 100$  only if there is  $\text{NO}_3+\text{NO}_2$  flux into the sediment  
b: Sum of  $\text{NO}_3+\text{NO}_2$  flux and amount of  $\text{NO}_3+\text{NO}_2$  needed to supply the measured rates of denitrification.  
c: Stoichiometric ratio of 2 mole of  $\text{O}_2$  needed to produce 1 mole of  $\text{NO}_3+\text{NO}_2$   
d: Sum of the positive fluxes of all N species ( $\text{NO}_3+\text{NO}_2$ ,  $\text{NH}_4$ ,  $\text{N}_2$ )  
e:  $\text{N}_2/\text{N}$  efflux \*100  
f: Respiratory Quotient = DIC/SOD

(A) Denitrification and N load



(B) DIC flux and Temperature



(C) SOD and temperature

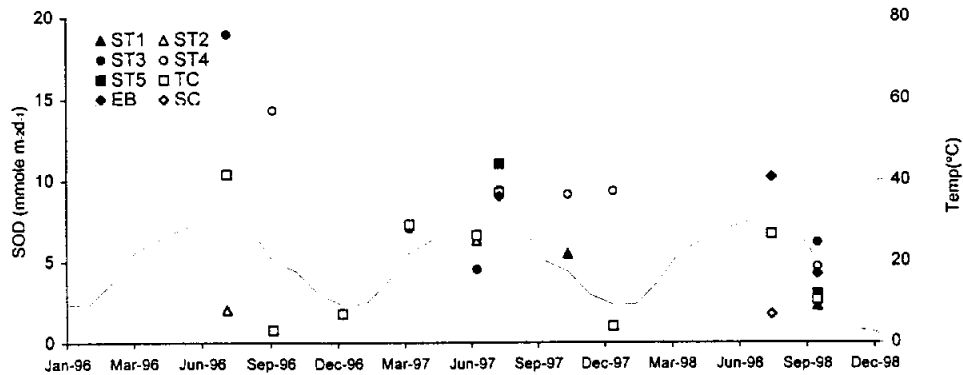


Figure 14. A. Temporal variation of denitrification rate (data points), N loading (dotted line), and temperature (solid line); B. DIC flux (data points) and temperature (solid line); and C. sediment oxygen demand (SOD; data points) and temperature ( $^{\circ}\text{C}$ ). Legends provide site identification.

stations were very high (4.32 and 3.21 mmole m<sup>-2</sup> day<sup>-1</sup> at St. 5 and East Bay, respectively). The high DIC flux and SOD (sediment oxygen demand) and NH<sub>4</sub> flux suggest significant rates of remineralization at these sites (Table 3). In the Galveston Bay system, the shallow water depth maintains the well-oxygenated bottom water despite the high SOD recorded at Station 4 (Table 3). This general statement may not hold true for Trinity mid-River stations, where marked O<sub>2</sub> depletion in bottom waters was observed during Aug. 1998.

The percent of denitrification supported by water column NO<sub>3</sub> + NO<sub>2</sub> versus that supported by in situ nitrification varies with time and space (Table 4). Water column NO<sub>3</sub> supported denitrification completely on several occasions. For example, during April 1997 and January 1998, when the water column NO<sub>3</sub> concentration was high (20.5 – 45 μM) due to increased freshwater discharge, NO<sub>3</sub> fluxes into the sediment support a significant fraction of denitrification activity at St. 3 (110%), St. 4 (55%) and Texas City (126%) (Table 4). Water column NO<sub>3</sub> concentration during January 1997 were lower than those measured in 1998 at St. 4 and Texas City. In January 1998, denitrification rates at St. 4 and Texas City were higher than those measured in January 1997, and the increased denitrification rates were reflected in a substantial NO<sub>3</sub> uptake by the sediments in 1998 relative to 1997.

Benthic NO<sub>3</sub> fluxes were almost always directed into the sediments, however the fluxes were usually small compared to the total N<sub>2</sub> flux. The NO<sub>3</sub> flux into the sediments, even if it is assumed that all fluxes were consumed via denitrification, supported, on average 25% denitrification (Table 4), suggesting that the main source of NO<sub>3</sub> for denitrification was from *in situ* nitrification (Kemp et al. 1990; Seitzinger 1988).

The seasonal variation in denitrification, temperature and nitrogen loading in Galveston Bay is shown in Fig. 14 (statistical results discussed later). As typically observed for any microbially mediated process, denitrification, the DIC flux and the SOD are well correlated with temperature fluctuations (Fig. 14). Nitrogen loading, however, did not fully explain the observed variability in denitrification rates. The highest denitrification rates corresponded to the time when nitrogen loading were the lowest. The general seasonal pattern of denitrification observed in many estuaries is a maximum in spring and a depression in mid summer (Koike and Sørensen 1988; Kemp et al. 1990). During spring or early summer, elevated temperatures lead to maximum denitrification rates because  $\text{NO}_3$  is still abundant. Spring plankton blooms rapidly exhaust riverine  $\text{NO}_3$  and denitrification is minimal during mid summer (Seitzinger et al. 1985; Jørgensen and Sørensen 1985). Oxygen availability also contributes to the mid summer depression. In many shallow coastal environments, denitrification is closely coupled to nitrification. Thus, nitrification and denitrification rates exhibit similar temporal trends (Koike and Sørensen 1988; Kemp et al. 1990). Sediment nitrification is generally dependent on the availability of  $\text{NH}_4$  and  $\text{O}_2$  (Henriksen and Kemp 1988). Since  $\text{NH}_4$  regeneration increases with temperature and nitrification is a temperature dependent microbial process, nitrification rates should be maximal during summer (Kemp and Boyton 1981). However, Kemp et al. (1990) found minimal nitrification (and denitrification) rates during summer time in Chesapeake Bay, which typically experienced summer time anoxia in bottom waters. Even if the bottom water does not become anoxic, the oxygen penetration depth is reduced because of increased SOD and this limits the volume of sediments in which nitrification can occur (Kemp et al. 1990).

Unlike Chesapeake Bay, a spring maximum and mid summer depression of denitrification was not observed in Galveston Bay. Even though some evidence of stratification is observed during summer, hypoxic/anoxic conditions are not common in Galveston Bay during the summer at present (except for example in Offats Bayou). When oxygen is not limiting, coupled nitrification-denitrification should be maximal during summer when the  $\text{NH}_4$  regeneration is highest (MacFarland and Herbert 1984; Jenkins and Kemp 1984). Kemp et al. (1990) observed summer time maximum concentrations of  $\text{NH}_4$  and  $\text{N}_2$  flux when  $\text{O}_2$  was not limiting. Though a seasonal trend in the  $\text{NH}_4$  flux was not obvious, remineralization activity (DIC flux) was highest during summer in the current study (Figure 14). In terms of spatial variability, average denitrification rates were highest at St. 1 in the Trinity River, with rates at the other core stations being similar (Fig. 15).

*Nitrification and benthic primary production.* Nitrification can be estimated from the observed  $\text{N}_2$  and  $\text{NO}_3$  flux data, assuming there was no  $\text{NO}_3$  or  $\text{NO}_2$  reduction to  $\text{NH}_4$  (Table 4; Zimmerman and Benner 1994; Kemp et al. 1990; Koike and Hattori 1979; Jenkins and Kemp 1984). We used stoichiometric ratios between nitrification and  $\text{O}_2$  consumption, to estimate  $\text{O}_2$  consumption related to nitrification. Finally, using benthic N flux data, we were able to calculate the percent of the benthic N flux present as  $\text{N}_2$  (Table 4, calculations explained on the table).

The average nitrification rate in Galveston Bay sediments is  $2.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; this value is higher than the Bay average denitrification rate ( $1.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). The average N flux from Galveston Bay sediments is  $2.5 \text{ mmol m}^{-2} \text{ d}^{-1}$  and, of that, 72% is  $\text{N}_2$  gas (Table 4). The nitrification rate ranged between 0 and  $9.6$

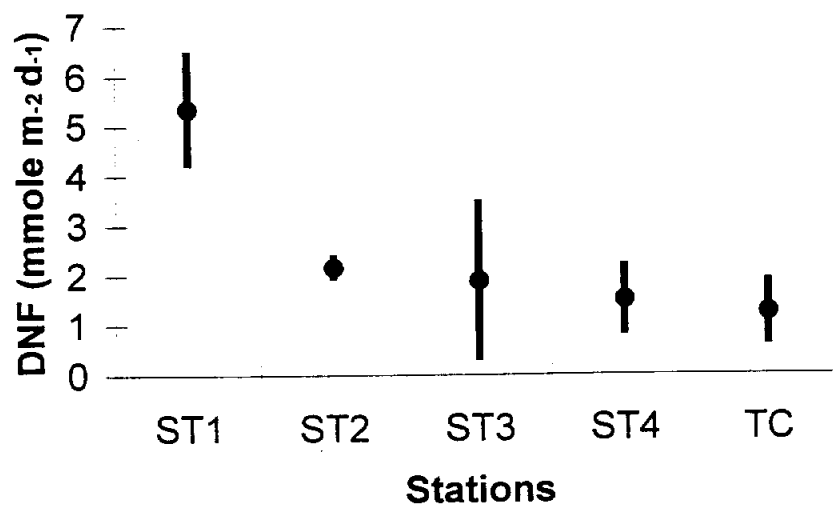


Figure 15. Annual average denitrification rate (circle) and standard deviation (bar) in Galveston Bay. See Figure 1 for the locations of stations. TC=Texas City. Stations are arranged from low (ST1) to high (TC) salinity.

mmole m<sup>-2</sup> d<sup>-1</sup> and exhibited distinct seasonal variation. The rate was high during summer (avg. = 4.7 mmole m<sup>-2</sup> d<sup>-1</sup>) and low during winter (avg. = 0.93 mmole m<sup>-2</sup> d<sup>-1</sup>). Interestingly, nitrification was low during Apr-97 (avg. = 1.2 mmole m<sup>-2</sup> d<sup>-1</sup>) when the water column NO<sub>3</sub><sup>-</sup> concentration was elevated due to high freshwater flow, as was the case during Jan-98 despite the higher than usual temperature and fairly high DIC flux.

The O<sub>2</sub> demand resulting from nitrification accounts for 109% of the measured SOD (Table 3, Table 4). In coastal environments, O<sub>2</sub> consumption by nitrification frequently accounts for 35% of SOD (Henriksen and Kemp 1988). Zimmerman and Benner (1994) report a value of 21 – 35% in Galveston Bay. Besides the fact that current estimation of O<sub>2</sub> consumption by nitrifiers is exceptionally high compared with other estuaries and previous estimates, a value exceeding 100% of SOD requires an additional O<sub>2</sub> source. Though the existing measurements of benthic primary production in Galveston Bay are not enough to delineate the annual average benthic primary production, the measured benthic primary production rates in Galveston Bay are comparable to water column primary production (see discussions above; Amstrong 1987; Zimmerman and Benner 1994; Krause-Jensen and Sand-Jensen 1998). We have observed O<sub>2</sub> production during chamber incubations at St. 3 and 4 during this study (Aug. 97, Nov. 97, Jan. 98, Apr. 98; Table 3). The oxygen production rate in November 1997 at Station 3 (15.9 mmole m<sup>-2</sup> day<sup>-1</sup>) was comparable to the highest SOD measured at the station. The high benthic chlorophyll *a* concentration also indicated active benthic primary production (An 1999).

Benthic microalgal production is important for sustaining benthic processes such as aerobic respiration, nitrification and denitrification (Risgaard-

Petersen et al. 1994; Tomaszek et al. 1997; Revsbech et al. 1980; Henriksen and Kemp 1988; Koike and Sørensen 1988; Anderson et al. 1984; An 1999). Recently, enhanced nitrification and denitrification coupling by benthic photosynthesis was reported (Tomaszek et al. 1997; Risgaard-Petersen et al. 1994), which contradicts Henriksen and Kemp's (1988) hypothesis that photosynthesis should inhibit coupled nitrification and denitrification.

Among the occasions when there were obviously high rates of benthic photosynthesis (see Table 3), no nitrification was observed only in Jan-98. The direction of the  $\text{NO}_3$  and  $\text{NH}_4$  benthic flux was into the sediment and the denitrification rate was the lowest measured. Although oxygen production was not detected at Texas City at the same time, the observed  $\text{O}_2$  and DIC flux (respiratory quotient = 11.7) and large influx of  $\text{NO}_3$  that exceeded the  $\text{NO}_3$  needs for observed denitrification suggest a high rate of primary production in this site (Table 3). These observations suggest that photosynthesis inhibited nitrification and coupled denitrification at this time. However, in Nov. 1997, there was a considerable amount of nitrification and denitrification. At this time, primary production did not seem to inhibit nitrification, though the predicted rate of photosynthesis should have been much higher than in Jan. 98 (the  $\text{O}_2$  production was an order of magnitude higher and there was DIC flux reduction compared to other seasons). No obvious environmental factors observed could account for this difference, other than the large freshwater input and associated increase in  $\text{NO}_3$  concentration in Jan. 98.

Despite the lack of net  $\text{O}_2$  production, the discrepancy between  $\text{O}_2$  needed for nitrification and measured SOD suggests that the benthic photosynthesis is required to support the rates of measured nitrification and coupled denitrification



in Galveston Bay. This link between photosynthesis and nitrification was not evident until the measurements were performed *in situ*. The effect of increased photosynthetic O<sub>2</sub> concentration on denitrification is complicated by the fact that though increased NO<sub>3</sub> availability stimulates denitrifying bacteria (by stimulating nitrification), it may also inhibit facultative anaerobic processes such as denitrification. A simple three box model was used to evaluate the overall effect of primary production on denitrification but these results are not presented here (An 1999).

*Conceptual framework and Modeling Results.* The sediment oxygen demand (SOD) has been used as a representative index of total remineralization activity (Smith and Teal 1973; Rowe et al. 1975). In typical estuaries, large portions of reduced chemicals produced during anaerobic respiration (sulfide or ferrous iron) are reoxidized within the sediments (Sørensen et al. 1979; Howes et al. 1984). When the reoxidation is complete, the SOD represents the total remineralization activity (Sørensen et al. 1979; Howes et al. 1984; Rowe et al. 1988). In this case, the SOD should balance the benthic dissolved inorganic carbon (DIC) flux, in other words, the ratio of DIC:SOD would be 1 (Rowe et al. 1988). DIC:SOD values greater than 1 indicate the importance of anaerobic respiration, while a ratio of 1 indicates that O<sub>2</sub> is the primary oxidant, even if part of the O<sub>2</sub> flux was consumed by inorganic oxidation, rather than organic oxidation.

The lowest DIC flux was measured at St. 4 in January 1997 (1.15 mmole m<sup>-2</sup> d<sup>-1</sup>) and the highest rate (40.5 mmole m<sup>-2</sup> d<sup>-1</sup>) was measured at St. 3 in July 1997 (Table 3). The highest SOD was measured at Sta. 3 in August 1996, but the DIC:SOD was less than 1. At Station 3, O<sub>2</sub> production during incubations was frequently observed. The seasonal and spatial variability of the SOD was usually

less than that of the DIC flux; average fluxes were  $17.7 \text{ mmole m}^{-2} \text{ d}^{-1}$  for DIC and  $6.9 \text{ mmole m}^{-2} \text{ d}^{-1}$  for the SOD. While the SOD is 50% higher than previous measurements in Galveston Bay (average SOD =  $4.6 \text{ mmole m}^{-2} \text{ d}^{-1}$ ; Zimmerman and Benner 1994), DIC production is about 4 times larger than the previous measurement ( $4.3 \text{ mmole m}^{-2} \text{ d}^{-1}$ ). The respiratory quotient (R.Q.) of the previous study was almost 1, which is the theoretical value reflecting a dominance of aerobic respiration processes (Rowe et al. 1988). The R.Q. values in the current study were usually greater than 1 (except Sta. 4 in January 1997, Table 3) and the average was 2.6. The highest value (11.3) was observed at St. 4 in January 1998.

High R.Q values (2 to 2.4) have been documented in many coastal environments (Dollar et al. 1991; Hargrave and Philips 1981; Joye et al. 1996). Hargrave and Philips (1981) suggested that a mismatch or time lag between anaerobic respiration (sulfate reduction) and oxidation of reduced compound (sulfide) might be responsible for the high R.Q. According to this explanation, however, the annual average R.Q. should approach 1 since the  $\text{O}_2$  debt produced during summer due to the high remineralization rate should be paid off sometime during winter.

Pyrite formation could also contribute to the high R.Q. If the sulfide produced during sulfate reduction is not re-oxidized and instead forms pyrite, the resulting DIC/SOD ratio would be high. Lin and Morse (1991) found a linear relation between pyrite formation and organic matter content in the Gulf of Mexico. Pyrite formation in Galveston Bay should not be a major contributor since most of the sulfide is reoxidized and the order of magnitude of DIC flux is much larger (Morse and Berner 1994). Another possibility that can alter the DIC flux is the occurrence of carbonate precipitation/dissolution. High rates of organic

matter degradation in the bottom water of coastal environments produce acidic conditions and can lead to carbonate dissolution (Boudreau 1987; McNichol et al. 1988; Zimmerman and Benner 1994). Generally, the magnitude of DIC production due to carbonate dissolution compared to that of remineralization is considered minor in coastal environments (Aller 1982; Boudreau and Canifield 1988). The depth profile of the inorganic carbon concentration of the sediment core from Station 4 (up to 60 cm) was variable but showed a constant trend with depth (Rowe unpublished data), which suggests that long term carbonate dissolution is not important at this station.

Nitrification, methane oxidation, and DOC flux could also contribute, to some degree, to modifying the R.Q. (Zimmerman and Benner 1994). Another potentially important process for the DIC and O<sub>2</sub> inventory at the sediment water interface is benthic photosynthesis. Benthic photosynthesis appears to be high in the Galveston Bay system. When the benthic photosynthesis is an important process, the observed DIC and O<sub>2</sub> flux will be the net result of organic matter decay and organic matter production (photosynthesis). Generally, DIC flux exhibits a positive relationship with the SOD. However, at St. 3, a negative relationship between the DIC and SOD was observed. An additional process influencing O<sub>2</sub> and CO<sub>2</sub> flux besides remineralization, e.g. photosynthesis, could explain this negative relationship.

Benthic photosynthesis consumes CO<sub>2</sub> and produces O<sub>2</sub>. When the R.Q. is exactly 1, and the photosynthetic quotient (P.Q. = O<sub>2</sub> production / CO<sub>2</sub> assimilation during photosynthesis) is also exactly 1, photosynthesis should not affect the R.Q. value. If the R.Q. is greater than 1, however, even if the P.Q. is 1, the R.Q. value will be increased by photosynthesis. For example, let

$$R.Q. = rCO_2/rO_2$$

( $rCO_2$ ,  $rO_2$ ;  $CO_2$  production and  $O_2$  demand during remineralization)

$$P.Q. = pCO_2/pO_2$$

( $pCO_2$ ,  $pO_2$ ;  $CO_2$  assimilation and  $O_2$  production during photosynthesis)

If  $R.Q. = P.Q. = 1$ , after the some amount ( $\phi$ ) of photosynthesis, the net fluxes of  $O_2$  and  $CO_2$  are:

$$CO_2 \text{ flux} = rCO_2 - \phi \times pCO_2$$

and

$$O_2 \text{ flux} = rO_2 - \phi \times pO_2$$

Since  $rCO_2 = rO_2$ ,  $pCO_2 = pO_2$ , the result is  $R.Q.=1$ .

However, if  $R.Q. = 1+\alpha$  ( $\alpha =$  positive number) and  $P.Q. = 1$ , after the same amount ( $\phi$ ) of photosynthesis, the net fluxes of  $O_2$  and  $CO_2$  are:

$$CO_2 \text{ flux} = rCO_2 - \phi \times pCO_2$$

and

$$O_2 \text{ flux} = rO_2 - \phi \times pO_2$$

Since  $rCO_2 = (1+\alpha) \times rO_2$ ,  $pCO_2 = pO_2$ , the resulting  $R.Q. = 1 + \alpha \times rO_2 / (rO_2 - \phi \times pO_2)$ . Since the term  $(rO_2 - \phi \times pO_2)$  is smaller than  $rO_2$ , the resulting  $R.Q.$  is larger than  $1+\alpha$ .

Furthermore, the  $P.Q.$  is known to be greater than 1. The theoretical value of  $P.Q.$  estimated from the reduction level of materials that plankton cells assimilate during photosynthesis is 1.03 – 1.3, depending on the nitrogen source (Falkowski and Raven 1997; Williams and Robertson 1991). When the  $P.Q.$  is greater than 1, the  $R.Q.$  value will be affected even more since the denominator

decreases while the nominator increases. The reported P.Q. range of natural plankton populations is from 0.5 to 3.5, having the bimodal distribution centered on 1.25-1.5 (when  $\text{NH}_4^+$  is nitrogen source) and 2.0-2.5 (when  $\text{NO}_3^-$  is nitrogen source) in their frequency distribution (Williams and Robertson 1991; Garcia and Purdie 1994).

To estimate the rate of photosynthesis that can explain the observed R.Q. values, a simple model was used to calculate the remineralization rate, the photosynthetic rate, nitrification and denitrification rates. Regeneration (R), photosynthesis (P), nitrification (N) and denitrification (D) were assumed to be the major processes affecting the fluxes (all rates are  $\text{mmole m}^{-2}\text{d}^{-1}$ ). The moles of ammonia needed to assimilate one mole of  $\text{CO}_2$  ( $\alpha$ ) during nitrification is known to vary from 5 to 100 (Zehnder and Stumm 1988). However, the overall result was not sensitive to this number and a value of 50 was chosen for  $\alpha$ . Molar ratios between  $\text{O}_2$  and  $\text{NH}_4$  ( $\beta$ ) and between  $\text{CO}_2$  and  $\text{N}_2$  production ( $\gamma$ ) of 2 and 2.5, respectively, were taken from Zimmerman and Benner (1994). A P.Q. of 1.8 was chosen (Williams and Robertson 1991; Garcia and Purdie 1994), assuming the source of N supporting photosynthesis was  $\text{NH}_4$  since it was well known that phytoplankton prefer  $\text{NH}_4$  to  $\text{NO}_3$  and it is unlikely that  $\text{NH}_4$  supply is limited in sediment. A C/N ratio (C2N) of 6 was chosen (Falkowski and Raven 1997) and two different values of R.Q. (R.Q.=1 and R.Q.=2) were compared in the calculation. The equations are:

$$\text{DIC flux} = R - P - N/\alpha + \gamma \times D \text{ ----- (1)}$$

$$\text{O}_2 \text{ flux} = - R/R.Q. + P \times P.Q. - \beta \times N \text{ ----- (2)}$$

$$\text{NH}_4 \text{ flux} = R/C2N - P/C2N - N \text{ ----- (3)}$$

$$\text{NO}_3 \text{ flux} = \text{Nit} - 2 \times D \text{ ----- (4)}$$

The four model equations can be solved simultaneously using the observed DIC, O<sub>2</sub>, NH<sub>4</sub> and NO<sub>3</sub> flux (Table 3). Except on two occasions (St. 4, Jan-97 and Texas City, Apr. 97), the equations produce values similar to the observed field data (Tables 3 & 5). The total (gross) remineralization rate was 2.3 (R.Q.=1) and 1.5 (R.Q.=2) times greater than the observed DIC flux. The modeled nitrification and denitrification rates did not exhibit a significant relationship to measured nitrification (estimated from the denitrification and NO<sub>3</sub> flux) or denitrification rates (from Table 3). However, the average modeled rate of nitrification (2.56 and 2.67 mmol m<sup>-2</sup> d<sup>-1</sup> for RQs of 1 and 2 respectively) was similar to the average nitrification rate obtained from field data (2.6 mmol m<sup>-2</sup> d<sup>-1</sup>). Modeled denitrification rates were about 60% of measured rates. Modeled nitrification and denitrification rates were not sensitive to variations in the R.Q.; however, total remineralization and photosynthesis were sensitive to the variations in the R.Q. (Table 5).

The model average photosynthetic rate was 22.7 (R.Q.=1) or 8.45 (R.Q.=2) mmol m<sup>-2</sup> d<sup>-1</sup>. The relationship between modeled remineralization rates and modeled photosynthetic rates was poor. The modeled photosynthetic rates were high between April and November and low in January. There was a decrease in photosynthesis in August, but trends were not clear.

The average ratio between photosynthesis and remineralization (P/R) was 0.53 when R.Q.=1 and 0.3 when R.Q.=2 (Table 5). When the R.Q. value was high, lower rates of photosynthesis relative to remineralization were needed to

Table 5. Calculated remineralization (R), photosynthesis (P), nitrification (N) and denitrification (D) rates ( $\text{mmole m}^{-2}\text{d}^{-1}$ ) from the equations described (See text). Calculations are based on the data in Table 3. *ND* : no data.

Month	Station	R.Q.=1					R.Q.=2				
		R	P	N	D	P/R	R	P	N	D	P/R
Oct-96	ST4	22.8	7.0	2.0	1.0	0.3	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
	Texas City	4.0	2.1	0.9	0.4	0.5	2.5	0.5	0.9	0.4	0.2
Jan-97	ST4	<b>negative solutions</b>					<b>negative solutions</b>				
	Texas City	7.7	4.0	0.6	0.3	0.5	4.7	1.0	0.6	0.3	0.2
Apr-97	ST1	74.4	46.7	4.8	1.1	0.6	45.8	18.1	4.8	1.1	0.4
	ST4	69.1	39.9	4.9	3.0	0.6	42.5	13.3	4.9	3.0	0.3
	Texas City	12.2	4.3	1.4	0.7	0.3	<b>negative solutions</b>				
Jul-97	ST2	56.7	32.4	4.0	2.0	0.6	34.9	10.6	4.0	2.0	0.3
	ST3	83.7	50.1	5.5	2.8	0.6	51.5	17.9	5.5	2.8	0.3
	ST4	23.0	4.9	2.9	1.3	0.2	23.0	4.9	2.9	1.3	0.2
	Texas City	32.6	16.4	1.8	0.9	0.5	20.1	3.9	1.8	0.9	0.2
Aug-97	ST3	36.1	25.6	1.3	0.6	0.7	22.2	11.7	1.3	0.6	0.5
	ST4	58.1	31.5	4.0	1.9	0.5	35.8	9.2	4.0	1.9	0.3
	ST5	61.5	32.3	3.8	1.4	0.5	37.9	8.6	3.8	1.4	0.2
	East Bay	45.8	23.4	2.4	1.2	0.5	28.2	5.8	2.4	1.2	0.2
	Texas City	30.2	13.8	1.9	0.9	0.5	18.6	2.2	1.9	0.9	0.1
Nov-97	ST1	72.6	40.7	3.1	1.8	0.6	44.7	12.8	3.1	1.8	0.3
	ST3	31.9	27.5	0.9	0.5	0.9	19.6	15.2	0.9	0.5	0.8
	ST4	32.1	14.3	1.4	0.6	0.4	19.7	2.0	1.4	0.6	0.1
Jan-98	ST3	22.1	14.7	1.4	1.0	0.7	13.6	6.2	1.4	1.0	0.5
	ST4	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
	Texas City	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
<b>Average</b>		<b>40.88</b>	<b>22.70</b>	<b>2.57</b>	<b>1.24</b>	<b>0.53</b>	<b>27.37</b>	<b>8.45</b>	<b>2.67</b>	<b>1.29</b>	<b>0.30</b>

explain the observed DIC and O<sub>2</sub> flux. How well the simplified relationships between various processes in the simple model equations represent the real processes occurring in the sediments is difficult to evaluate. The result of this simple exercise does show, however, the importance of photosynthesis in shaping, at least in a short time scale, the fluxes of DIC and O<sub>2</sub> in shallow estuarine sediments. This exercise also underscores the importance of *in situ* incubation experiments. For example, the effect of photosynthesis could not have been observed in the previous study of Zimmerman and Benner (1994) since their flux measurements were performed in the dark.

*Environmental controls on Denitrification.* Figure 16 shows a simplified conceptual relationships between various processes and relevant materials in coastal sediments, with an emphasis on denitrification. River discharge introduces organic (labile organic C) and inorganic materials (NO<sub>3</sub>) that fuel denitrification. At the same time, however, river discharge decreases salinity (which should increase N removal; Joye, Lee and Carini, in preparation) and reduces the residence time of the system (which should decrease N removal; Nixon et al. 1996). Increased temperature will enhance all microbial processes, including denitrification and benthic photosynthesis (Jørgensen 1977; Koike and Sørensen 1988; Henriksen and Kemp 1988). Primary producers and nitrifying consume NH<sub>4</sub> produced during organic matter degradation. Whether benthic primary producers compete with nitrifiers for NH<sub>4</sub> (thereby inhibiting nitrification) or provide O<sub>2</sub> for them (thereby enhancing nitrification) (Henriksen and Kemp 1988) appears to vary seasonally in Galveston Bay. Increased O<sub>2</sub> availability due to benthic primary production has been shown to enhance nitrification in other systems (Risgaard-Petersen et al. 1994) as well as



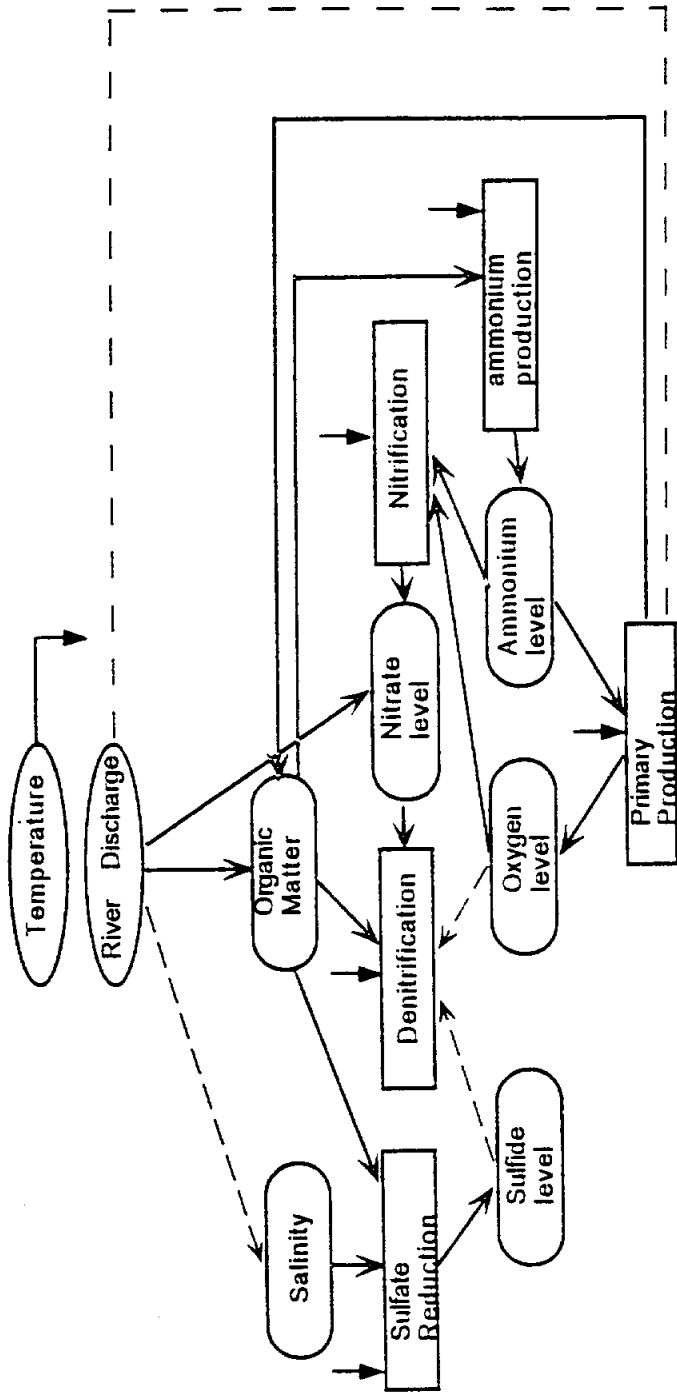


Figure 16. Conceptual relationships between various processes emphasizing denitrification. Solid arrows represent positive effect, white broken arrows represent negative effect.

in this system (discussion above; An 1999; Joye and An, in preparation). Whether primary production inhibits or enhances nitrification and nitrification-denitrification coupling is regulated by the balance between photosynthesis and respiration. High rates of photosynthesis could stimulate nitrification, but at the same time inhibit denitrification (high  $[O_2]$  inhibits denitrification (Tiedje et al. 1989). The interaction between benthic photosynthesis and nitrogen cycling is therefore complex and varies on daily as well as seasonal/annual time scales.

Joye and Hollibaugh (1995) proposed sulfide inhibition of nitrification as a mechanism to explain the increased coupling efficiency between nitrification and denitrification in freshwater sediments. Increased salinity will enhance sulfate reduction (sulfide production rate) and sulfide concentration in sediment. Direct (toxic to denitrifiers) and indirect effects (via reduced nitrification) of increased sulfide concentration on denitrification should result in decreased rates of activity. The overall effect of various environmental factors, such as temperature and freshwater discharge, on denitrification will be determined by the presence of various processes and compounds that may enhance or inhibit the denitrification complicated ways.

*Statistical analysis.* Table 6 presents the result of an Analysis of Variance (ANOVA) of the process and environmental data collected during this study. Water temperature explained the 68, 26 and 42% variability of denitrification, SOD and DIC flux respectively (Table 6). Salinity variability did not significantly relate to any process. Total nitrogen loading and percent sand accounted for about

Table 6. Percent of variance accounted for by environmental factors.  
 Data are pooled from all stations and seasons.

Environmental factors	Denitrification	SOD	DIC flux
Water temperature	68	26	42
Salinity	0	0	0
Total nitrogen loading	9	6	6
Percent sand	11	5	4
Chlorophyll	0	15	3

10% of the variability of denitrification. The variability of SOD was well explained by sediment chlorophyll *a* concentration, as opposed to denitrification and/or DIC flux. Since many environmental variables were inter-dependent, it was difficult to elucidate the effect of individual variables.

Principal component analysis (PCA) was used to reveal independent (orthogonal) sets of factors that can be related to each variable or process (Sneath and Sokal 1973; Figure 17). Three factors explained 82% of the variability and were used to coordinate the variables and processes (Figure 17). Factor one explained 44% of the variability and was positively correlated with temperature ( $r = 0.82$ ), DIC flux (0.90) and denitrification (0.80) and negatively related with salinity (-0.47) and  $\text{NO}_3$  concentration (-0.24). Factor 1 appeared to represent season (or temperature). Factors 2 and 3 explained 23.4% and 14.6% of variability, respectively.  $\text{NO}_3$  concentration had a high positive (0.90) correlation with factor 2. Sediment oxygen demand also had positive correlation (0.45) but salinity (-0.7) had a negative relationship with Factor 2. Factor 2 may represent freshwater input. Sediment chlorophyll concentration had high positive correlation with Factor 3 while DIC flux had negative relations. Factor 3 appears to represent the benthic photosynthesis. Denitrification,  $\text{NO}_3$  concentration, salinity and sediment oxygen demand had positive relationships with Factor 3.

We believe the factors derived from the PCA can be related to important environmental conditions that regulate benthic remineralization processes. Sediment grain size is another important variable but since this variable remains stable for short periods of time (i.e. months), it was not included in this analysis.

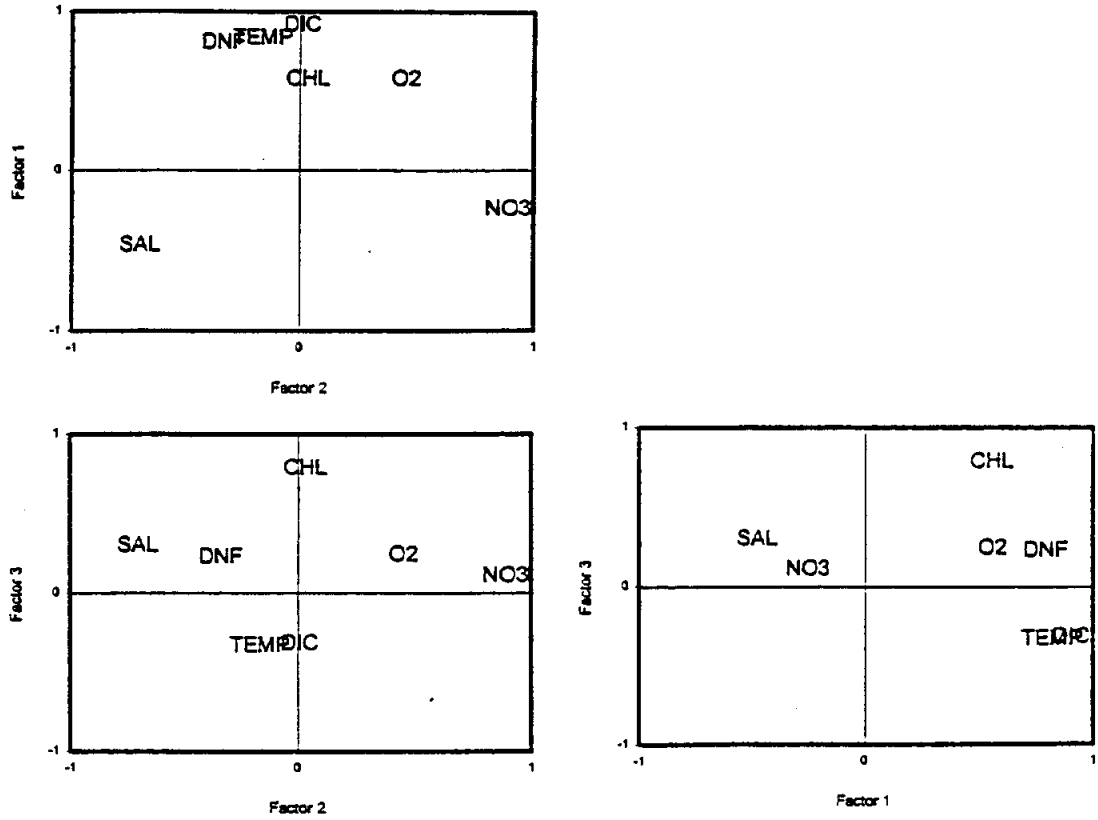


Figure 17: Results of the PCA analysis. DNF: denitrification; O2: sediment oxygen demand; DIC: DIC flux; CHL: sediment chlorophyll *a*; SAND: % sand; LOAD: freshwater input; TEMP: temperature; and, SAL: salinity.

The seasonal change of temperature (Factor 1) was the most important variable; all the benthic processes exhibited a strong positive relationship to it.

Freshwater loading (Factor 2) does not seem to affect the benthic processes very much, although the SOD was positively correlated with it. Denitrification had a negative relationship with freshwater input but the correlation was weak. The correlation between benthic primary production (Factor 3) and benthic processes was also weak. Denitrification rates exhibited a positive correlation to benthic production, which is consistent with the field and modeling results.

*Galveston Bay N Budget.* The bay-wide denitrification rate in Galveston Bay was estimated from the temperature and denitrification relationship (Joye and An 1998; An 1999). Since temperature was the environmental variable explaining most of the variability of denitrification, temperature dependent regression equations were derived for fine (% sand < 80) and coarse (% sand > 80) sediments to estimate the monthly averaged denitrification rates in Galveston bay. The areal distribution of each sediment type in Galveston Bay was estimated from USGS maps. Average water temperature for each month was obtained from TNRCC. The monthly averaged denitrification rates for each sediment type were then summed to obtain monthly bay-wide denitrification rates. As such, the average denitrification rate in Galveston Bay was  $8.3 \times 10^7$  mol N month<sup>-1</sup>. Figure 18 shows the 10 year averaged monthly values of N loading, denitrification and % load loss via denitrification. Nitrogen removal via denitrification averaged approximately 52% of total N loading. Nitrogen loading was high during spring but denitrification was not efficient at removing N at that time. During summer,

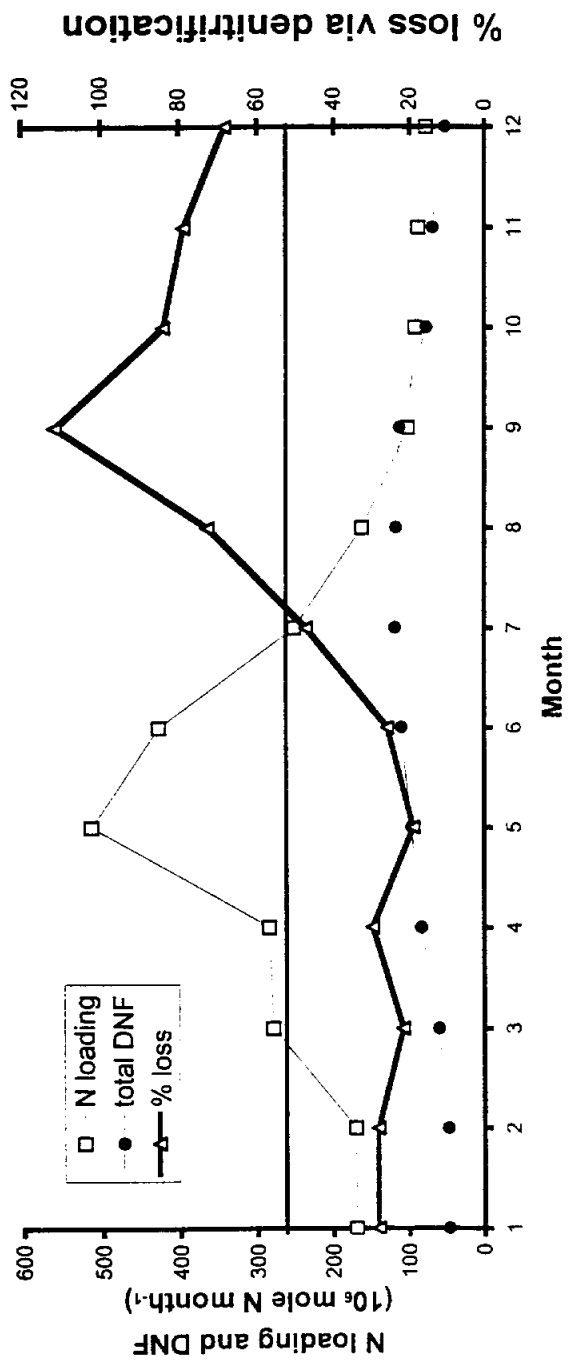


Figure 18. Whole system denitrification, nitrogen loading and % loss via denitrification in Galveston Bay. The rate was calculated using the denitrification rate in the relationship:  $DNF = a \times 10(b \times \text{temp})$ . Horizontal line represents the average removal (%).

when N loading decreased, denitrification rates increased, resulting in efficient removal of up to 110% of N loading.

The removal rate reported here is similar to that previously reported for Delaware Bay (Seitzinger 1988) and the Tama Estuary, Japan (Nishio et al. 1982), but is much higher than previous estimates for Galveston Bay (DNF = 14% of N loading; Zimmerman and Benner 1994). Zimmerman and Benner (1994) used dark, laboratory incubations (following a 10 day pre-incubation) to determine denitrification rates. This pre-incubation probably altered coupling and interaction between photosynthesis-nitrification-denitrification. Furthermore, enhanced nitrification-denitrification coupling driven by benthic primary production would not have been observed using this assay technique since sediment cores were incubated in the dark (Zimmerman and Benner 1994). In all likelihood, denitrification rates determined in their study underestimated the true *in situ* activity.

Nixon et al. (1996) presented a relationship between hydraulic residence time and denitrification. According to this relationship, N loss by denitrification in Galveston Bay should approximate 35% of total N loading. Our calculated removal rate is about 17% higher than that. Enhancement of denitrification by benthic primary production in Galveston Bay may serve to stimulate N removal and complicate the interaction between hydraulic residence time and denitrification.

Table 7 shows the annual N budget for Galveston Bay (Brock et al. 1996). In the Brock et al. report, N loss by denitrification ( $3680 \times 10^6$  g N year<sup>-1</sup>) was based on data from Zimmerman and Benner (1994). The loss increases from 3680



Table 7. Annual nitrogen budget for the Galveston Bay system, 1988 to 1990. Data from Table 12 of Brock (1996); table been adapted from An (1999). Units in  $10^6$  g N yr<sup>-1</sup>.

	1988	1989	1990	Average	Std. Dev.
<b>Input</b>					
Fresh water inflow	19500	43550	49250	<b>31525</b>	15790
Nitrogen fixation	560	560	560	<b>560</b>	0
Tidal Entrainment	2330	2440	2240	<b>2385</b>	100
<b>Total</b>	<b>22390</b>	<b>46550</b>	<b>52050</b>	<b>34470</b>	<b>15778</b>
<b>Loss</b>					
Outflow	-25420	-42380	-38590	<b>-33900</b>	8902
Denitrification	-3680	-3680	-3680	<b>-3680</b>	0
Burial in sediment	-690	-2280	-2630	<b>-1485</b>	1034
Fisheries, Fish migration	-770	-1070	-1430	<b>-920</b>	330
<b>Total</b>	<b>-30560</b>	<b>-49410</b>	<b>-46330</b>	<b>-39985</b>	<b>10112</b>
Water column storage	170	270	-360	<b>220</b>	339
<b>Remainder</b>	<b>-8000</b>	<b>-2590</b>	<b>5370</b>	<b>-5295</b>	<b>6725</b>

to  $14000 \times 10^6$  g N year<sup>-1</sup> and remainder decreases from -1740 to  $-12063 \times 10^6$  g N year<sup>-1</sup> when the denitrification data obtained in study are used (Table 3). The negative balance might reflect the decreased total N loading to Galveston Bay since 1973 (Shiple & Kiesling 1994) or other internal inputs (e.g. N fixation) that were not measured during our study. The negative balance might also result from an underestimation of sources and/or an overestimation of losses (Brock et al. 1996). These trends could not be confirmed since the N budget calculation was based on relatively short-term data (1988-1990; Brock et al. 1996). Brock et al. (1996) suggested the source of bias in budget calculation might be the “entrainment rate” used in budget calculation. The “entrainment rate” was used to estimate the amount of coastal water mixed with bay water (Brock et al. 1996). The range of variability of the remainder using different “entrainment rate” was about  $30000 \times 10^6$  g N year<sup>-1</sup> (Brock et al. 1996). It is clear that errors in the estimated entrainment rate could ‘erase’ the N deficit noted above: The difference of remainder between the former budget calculation and the budget calculation using current denitrification measurement lies within this range of variability. According to current study, the importance of denitrification as a N sink process in Galveston Bay is greater than previously estimated. More detailed studies of the sources and sink terms of total N in Galveston bay are necessary to construct an improved N budget and confirm the trends speculated upon here.

#### **IV. Concluding Remarks**

The method we employed to determine denitrification rates in Galveston Bay sediments was relatively simple and it provided us with *in situ* rate estimates of benthic processes in Galveston Bay. The relatively small sample volume (2 ml)

required for dissolved gas analyses permitted replication of samples, minimizing the influence of signal dilution. Using benthic incubation chambers, the *in situ* method allowed us to observe interactions between denitrification and benthic photosynthesis. The study of the N processing in sediments has usually employed dark incubations, such incubations do not permit the effect of benthic primary production on N cycling in shallow estuaries and could result in erroneous estimates of N cycling rates in sediments.

The average Secchi depth in Galveston Bay was 0.65 m (10 year average,  $n=1500$ , standard deviation = 0.4). The depth of the euphotic zone, estimated from the Secchi depth, was 1.77 to 2.5 m and was similar to the average water depth (1.74 m). Despite this, benthic chlorophyll concentration in the surface sediment of Galveston Bay was high ( $500 \text{ mg Chl } a \text{ m}^{-2}$ ) and the measured benthic primary production is comparable to rates water column primary production. Results obtained in this study infer a positive feedback between benthic photosynthesis and coupled nitrification-denitrification. This feedback could serve as an important regulator of N cycling in estuarine sediments. Studies such as those described here should be carried out in other estuarine environments to evaluate the generality of this conclusion.

Dissolved  $\text{N}_2$  and dissolved inorganic carbon fluxes from Galveston Bay sediments ranged from 0.6 to 4.6 (avg. =1.8,  $n=24$ , STD = 1.1) and from 1.2 to

40.5 (avg.=17.7, n = 21, STD = 12) mmol m<sup>-2</sup> d<sup>-1</sup>, respectively. Both DIC and N<sub>2</sub> fluxes exhibited a summer maximum. The bottom waters of Galveston Bay were well-oxygenated even during summer and nitrification rates estimated from the denitrification and NO<sub>3</sub><sup>-</sup> fluxes exhibited a summer maximum. Elevated denitrification rates observed during summer resulted from the stimulation of nitrification-denitrification coupling by high rates of benthic photosynthesis and the consumption of O<sub>2</sub> by respiration (and nitrification). Benthic photosynthesis provided the O<sub>2</sub> required to support aerobic respiration and nitrification in Galveston sediment. Most of the NO<sub>3</sub><sup>-</sup> used for denitrification (97%) was supplied from *in situ* nitrification. The proportion of denitrification supported by water column influx was higher during winter and spring, when the water column NO<sub>3</sub> concentration was high, than during summer and fall, when the water column NO<sub>3</sub> concentration was low.

The ratio between the DIC flux and the SOD was high (2.6) in Galveston Bay sediments. Model results suggest that when benthic primary production is important, the observed DIC and O<sub>2</sub> flux reflect the net result of organic matter decay and photosynthesis. Although other processes such as carbonate precipitation/dissolution and pyrite formation might influence these fluxes and the flux ratio, benthic primary production could produce the high ratio between DIC flux and SOD in Galveston Bay.

Temperature was the most significant factor explaining the variability in denitrification rates in Galveston Bay. Denitrification rates were higher in fine-grained compared to coarse-grained sediment. Bottom water  $\text{NO}_3$  concentration was not significantly related to denitrification rates. Though freshwater stations exhibited higher denitrification rates generally, salinity did not explain a significant fraction of the variability in denitrification rates. Principal component analyses showed that season (temperature fluctuation), freshwater discharge, and primary production were important environmental factors influencing benthic processes and denitrification rates in Galveston Bay.

The average N loading rate (monthly average) to Galveston Bay during this study was  $170 * 10^6 \text{ mol N month}^{-1}$ . Over an annual cycle, denitrification removed 52% of the annual N loading to Galveston Bay. While N loading was highest during spring and lowest during summer, denitrification rates were lowest during spring and highest during summer. Therefore, denitrification was less effective in removing N during winter and spring. During summer, when denitrification rates were highest and N loading was lowest, denitrification removed to 110% of the N load. It is difficult to estimate the specific source of N denitrified during benthic chamber incubations. For example, evaluating whether the denitrified N was delivered from the riverine end member, deposited on the Bay surface via atmospheric precipitation, or introduced to the system from the marine end member would require a specific tracer (perhaps stable N isotopes)

that was unique for each 'source' of N. Nonetheless, we can state that denitrification rates in this system could remove > 50% of the annual riverine N load delivered to the system. Future studies should focus on determining the specific sources of N that fuel denitrification in the Galveston Bay system

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