Denitrification in Galveston Bay
Final Report

A final project report submitted to the
Texas Water Development Board

by:

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Table of Contents

List of Figures and Tables:

Preface and Acknowledgements

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_2) fixation, ammonification, N assimilation, nitrification, dissimilatory nitrate reduction to ammonium, and denitrification (Blackburn and Sørensen 1988; Cole and Ferguson 1988). Physical dynamics, such as advection, sedimentation, and sediment resuspension, also contribute to the movement of N between compartments; however, microbially mediated processes ultimately transform N between forms and thus regulate the magnitude of N loss from an ecosystem (via denitrification). Dinitrogen gas can serve as a nutritional N source to only a limited suite of microorganisms (N_2 fixers; Knowles 1982; Howarth et al. 1988; Zumft et al. 1988). 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_2 or nitrous oxide (N_2O). Denitrifying bacteria respire nitrate when oxygen (O_2) concentrations are below 20 μM; Knowles 1982; Tiedje et al. 1989); however, some O_2 tolerant denitrifiers are known (Robertson and Kuenen 1991).

Since denitrification is a sink for N, it is important to identify the environmental and physiological factors that regulate the process. Denitrification is frequently controlled by the NO_3 concentration but temperature and the concentration of organic carbon, O_2 and hydrogen sulfide (HS^-) 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_3

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^{-2} d^{-1} (Seitzinger 1988), while

nitrification rates range between 0 - 5 mmol N m^{-2} d^{-1} (Henriksen and Kemp

1988). Spatio-temporal variations in temperature, organic carbon supply, and O_2

and HS^- concentration may affect nitrification and, thus indirectly influence

denitrification (Henriksen and Kemp 1988; Joye and Hollibaugh 1995) or coupling

between nitrification and denitrification (Nishio et al. 1983; Jenkins and Kemp

1984; Christensen et al. 1987; Caffrey and Kemp 1990; Kemp et al. 1990;

Binnerup and Sørensen 1992).

The Galveston Bay 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 μmol N m^{-2} 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 mmol N m^{-2} d^{-1} from benthic flux O:N stoichiometry. This estimate of denitrification suggest that >50% of N mineralized in sediments is lost as N$_2$ gas and, more importantly, that 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.
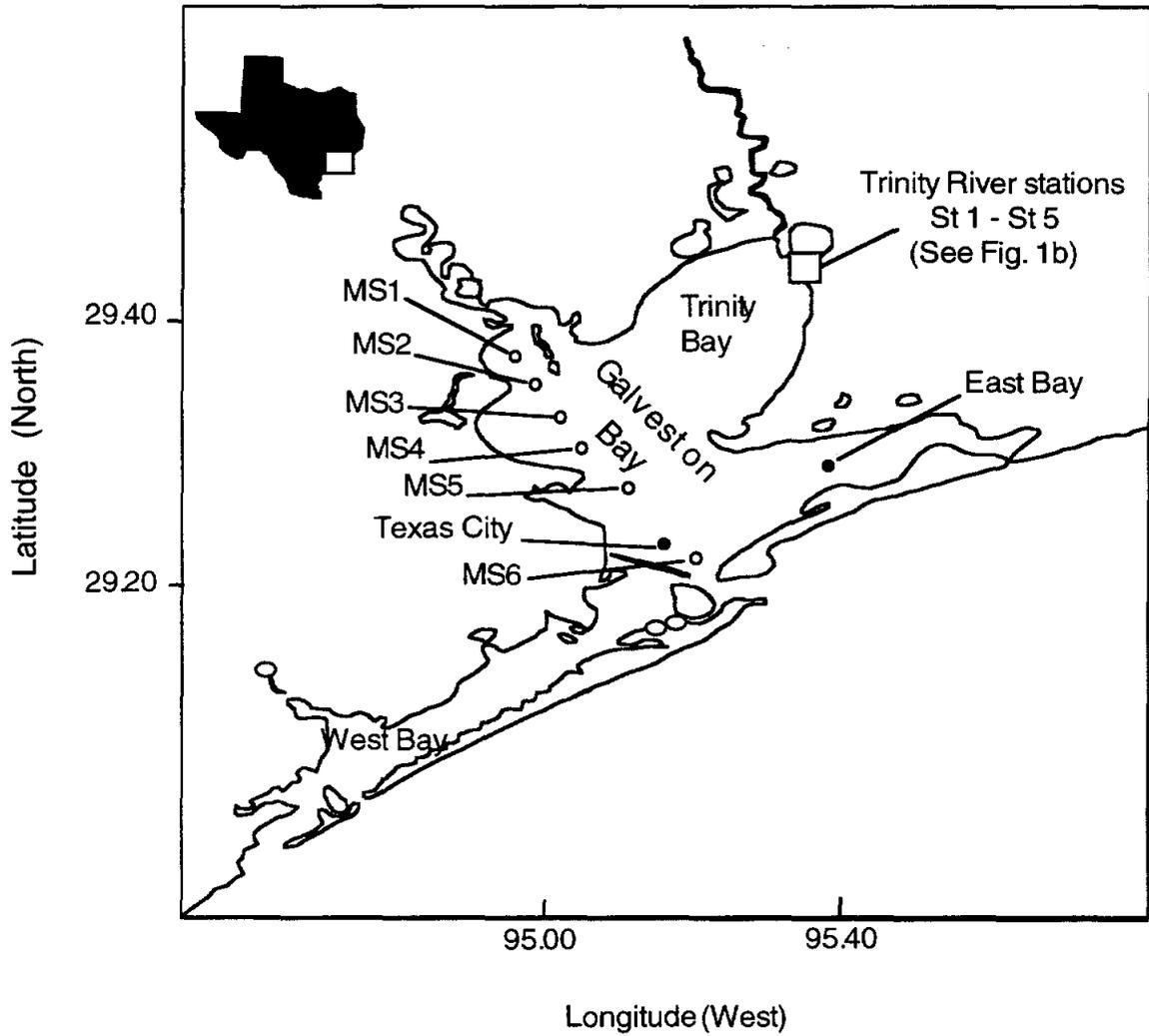
Figure 1(a). Sampling Stations in Galveston Bay. MS 1-6 represent
the monitoring stations of the TNRCC. See Fig. 1b for detail map of
the Trinity River chamber and transect stations.
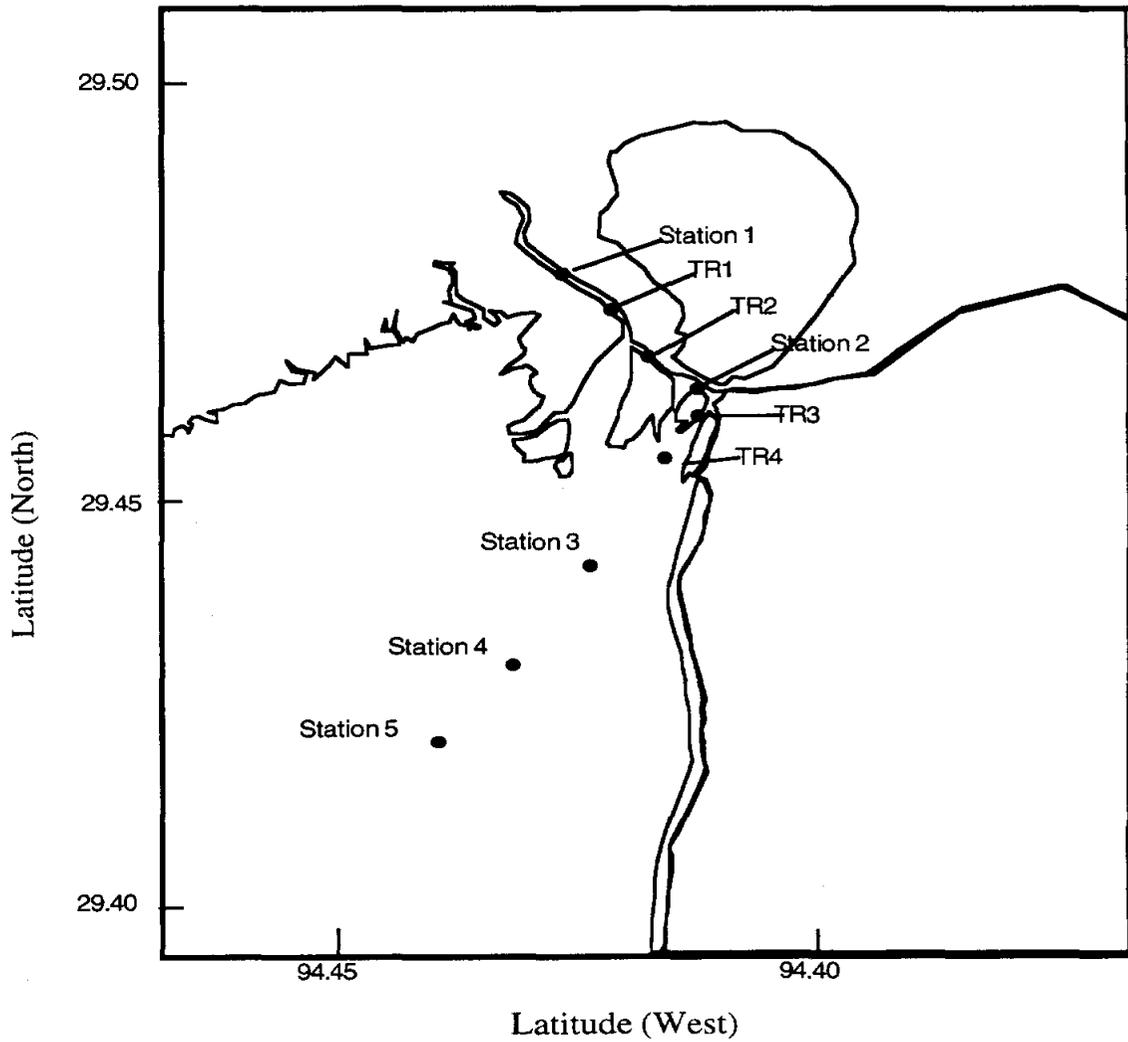
Figure 1(b). Detail map of the Trinity River chamber (stations 1-5) and transect (TR 1 - 4) stations. [Redrawn from Joye and An (1997)].

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_2) 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. $NO_3 + NO_2$ and PO_4 concentration were determined using standard methods on an Alpkem FlowSolution 3000 Autoanalyzer (Joye et al. 1999). NH_4 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_2 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 stablized 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_2 and N_2 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_2/O_2 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_2, N_2, 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_2 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_2 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
Location	Longitude		94.43.063		94.41.511		94.42.828		94.43.667		94.44.063		94.49.659		94.37.823	
	Latitude		29.47.700		29.46.348		29.43.771		29.42.613		29.41.995		29.23.516		29.30.650	
Depth (m)			2.1		3		3.6		1.5		1.5		4.5		2.1	
Temp. (°C)	1996	June	28	28	-	-	28.5	27	28.5	28.2	-	-	-	-	-	-
		July	31.3	30.6	32	30	30.5	27.5	31	-	-	-	-	-	-	-
		Aug.	28.3	28	29	28	28.2	26.9	28.5	28	-	-	-	-	-	-
		Oct.	-	-	-	-	-	-	18.5	17	-	-	21.5	20.1	-	-
	1997	Jan	14.3	14.3			14	14.1	13.8	13.8	-	-	14.8	15.2	-	-
		Apr	18.7	18.7	19.3	19.3	20.1	19.9	18.9	18.7	-	-	20	19.7	-	-
		July	30.6	30.6	32	29.7	32.8	32.8	29.6	29.6	-	-	31.4	31.2	-	-
		Aug.	31.6	30.7	27.8	27.9	27.9	26.9	31.6	31.6	31.2	31.2	31.1	31	31.6	30.8
		Nov.	15.6	15.6	15.4	15.4	15.3	15.3	129	12.9	-	-	-	-	-	-
	1998	Jan.	14.5	-	14.2	-	14.3	14.4	14.1	14.2	-	-	14.5	15.2	-	-
		Apr.														
		Aug.	32	31.7	31.2	30.1	31.2	30.4	31.8	31.2	-	-	33.2	31.1	30.2	30.8
		Nov.	21.7	21.8	21.9	21.9	21.7	21.6	22.2	20.1	19.6	19.6	21.9	21.7	22.1	22.1
Salinity (ppt)	1996	June	-	0	-	-	-	-	-	-	-	-	-	-	-	-
		July	0	0	1.5	-	10	12	15	-	-	-	16	17	-	-
		Aug.	0	0	0	0	0	0	-	-	-	-	-	-	-	-
		Oct.	0	0	0	0	0	0	-	-	-	-	-	-	-	-
	1997	Jan	0	0	0	0	0	0	1.5	1.5	-	-	6.3	7.2	-	-
		Apr	0	0	0	0	0	0	0	0	-	-	0.9	1.2	-	-
		July	0	0	0	0	0	0	0.4	0.4	-	-	20.9	23.8	-	-
		Aug.	0	0	3.3	3.4	4.1	4.1	5.2	5.3	7.6	7.8	29.6	29.8	12.2	12.5
		Nov.	0	0	0	0	0.4	0.4	0.4	0.4	-	-	-	-	-	-
	1998	Jan.	0	0	0	0	0	0	0	0	-	-	6	13	-	-
		Apr.														
		Aug.	3.93	3.95	5.52	7.05	11.18	11.93	12.22	12.18	-	-	28.2	31.3	19.9	20.4
		Nov.	0	0	0	0	0	0	1.6	5.8	4.6	6.4	13.7	19.5	11.3	11.4
O_2 (ml/L)	1996	June	9.8	6.5	-	-	9.1	6.6	7.7	6.1	-	-	-	-	-	-
		July	7.2	6.4	8.1	5.0	5.6	4.2	-	6.6	-	-	-	-	-	-
		Aug.	6.8	5.2	-	5.4	10.8	7.5	8.6	5.8	-	-	-	-	-	-
		Oct.	-	-	-	-	-	-	8.7	7.9	-	-	8.4	6.2	-	-
	1997	Jan	10.2	10	-	-	10	10	10.2	10.2	-	-	9.2	8.5	-	-
		Apr	7.7	7.6	7.6	7.5	8.3	7.9	8.3	8.2	-	-	8.3	7.8	-	-
		July	6.8	5.6	6.7	4.3	6.3	6.2	6.9	6.6	-	-	7.1	5.7	-	-
		Aug.	7.3	4.6	6.7	6.4	7.5	7	6.5	6.3	6.4	5.7	5.5	5	8.9	6.5
		Nov.	9.8	9.3	9	9.1	9.1	9.1	9.8	9.6	-	-	-	-	-	-
	1998	Jan.	10	9.9	9.5	9.3	10.2	10.2	10.5	10.5	-	-	9.5	8.7	-	-
		Apr														
		Aug.	6.7	5.4	5.3	3.2	5.2	3.6	5.9	5.6	-	-	6.4	6.3	6.6	5.5
		Nov.	6.6	6.0	6.5	6.3	6.3	6.2	7.1	5.6	7.3	5.8	7.4	5.9	8.2	7.3

Table 1 (Continued)

			OB Surface	OB Bottom	1 Surface	1 Bottom	2 Surface	2 Bottom	3 Surface	3 Bottom	4 Surface	4 Bottom
Location	Longitude		94.50.87		94.42.551		94.42.275		94.41.479		94.41.991	
	Latitude		29.16.91		29.47.41		29.46.907		29.45.947		29.44.864	
Depth (m)			5.1		3.6		3.6		3.6		3	
Temp. (°C)	1996	June	-	-	-	-	28	28	-	-	-	-
		July	-	-	31	31.5	30.5	30.5	31.5	32	31.1	28.2
		Aug.	28	27.2	-	-	-	-	-	-	-	27
		Oct.	23	22.5	-	-	-	-	-	-	-	-
	1997	Jan.	-	-	14.3	14.3	14.2	14.3	14.2	14.2	14	14.2
		Apr.	-	-	-	-	-	-	-	-	-	-
		July	-	-	31.5	29	31.5	29.6	-	-	31.3	29.9
		Aug.	-	-	31.3	31.1	31.2	31	30.7	30	29.7	28.9
		Nov.	-	-	15.5	15.5	15.5	15.5	15.5	15.5		
	1998	Jan.	-	-	14.3	14.3	14.2	14.3	14.1	14.3	14.2	14.2
		Apr.	-	-								
		Aug.	-	-	32.4	32.2	32.2	32	31.3	30.1	32	30.6
		Nov.	-	-	21.8	21.8	21.9	21.8	21.8	21.8	21.8	21.8
Salinity (ppt)	1996	June	-	-	-		3		-		-	
		July	32	34	-	-	0	-	-	-	0	10
		Aug.	-	-	-	-	-	-	-	-	-	-
		Oct.	-	-	-	-	-	-	-	-	-	-
	1997	Jan.	-	-	0	0	0	0	0	0	0	0
		Apr.	-	-	-	-	-	-	-	-	-	-
		July	-	-	0	0	0	0	-	-	0	0
		Aug.	-	-	0	0	0	0	0.4	2.7	1.1	2.3
		Nov.	-	-	0	0	0	0	0	0	-	-
	1998	Jan.	-	-	0	0	0	0	0	0	0	0
		Apr.	-	-								
		Aug.	-	-	3.12	3.13	3.54	3.6	6.54	8.78	9.38	10.58
		Nov.	-	-	0	0	0	0	0	0	0	0
O_2 (ml/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	3.9
		Aug.	10.2	4.3	-	-	-	-	-	-	9.3	7.6
		Oct.	8.2	4.2	-	-	-	-	-	-	-	-
	1997	Jan.	-	-	10.3	9.8	10.3	9.5	10.1	9.8	10.3	9.7
		Apr.	-	-	-	-	-	-	-	-	-	-
		July	-	-	7.3	4.7	7.3	4.6	-	-	8.2	5.4
		Aug.	-	-	7.2	5.9	6.5	6	7.7	5.4	7.7	5.6
		Nov.	-	-	10	9.5	9.2	9	9.2	9	-	-
	1998	Jan.	-	-	9.8	9.7	10.1	10.1	9.7	9.7	9.6	
		Apr.	-	-								
		Aug.	-	-	6.0	5.1	5.6	5.2	5.0	3.6	6.1	4.0
		Nov.	-	-	6.7	6.3	7.1	6.3	6.9	6.4	6.7	6.5

The depth distribution of temperature, salinity, pH and dissolved O_2 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_2 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_2 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_2 depletion at depth, particularly at mid-River sites (Fig. 2 G-I; Fig. 3). Dissolved O_2 % 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_2 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_2 concentration (Joye and An 1998).

The depth distribution of temperature, salinity, pH and dissolved O_2 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_2 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 dissoved O_2 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 dissoved O_2 over
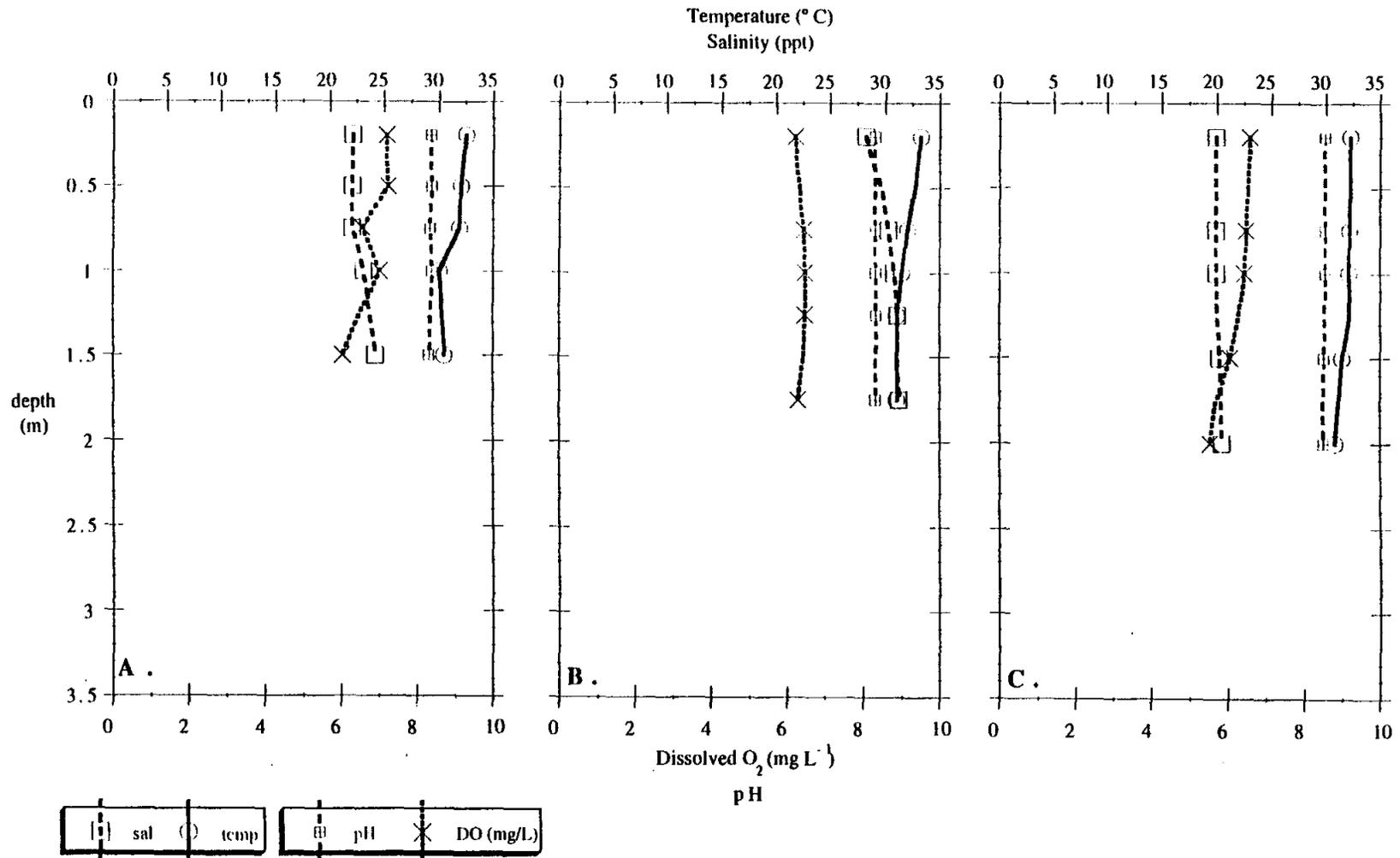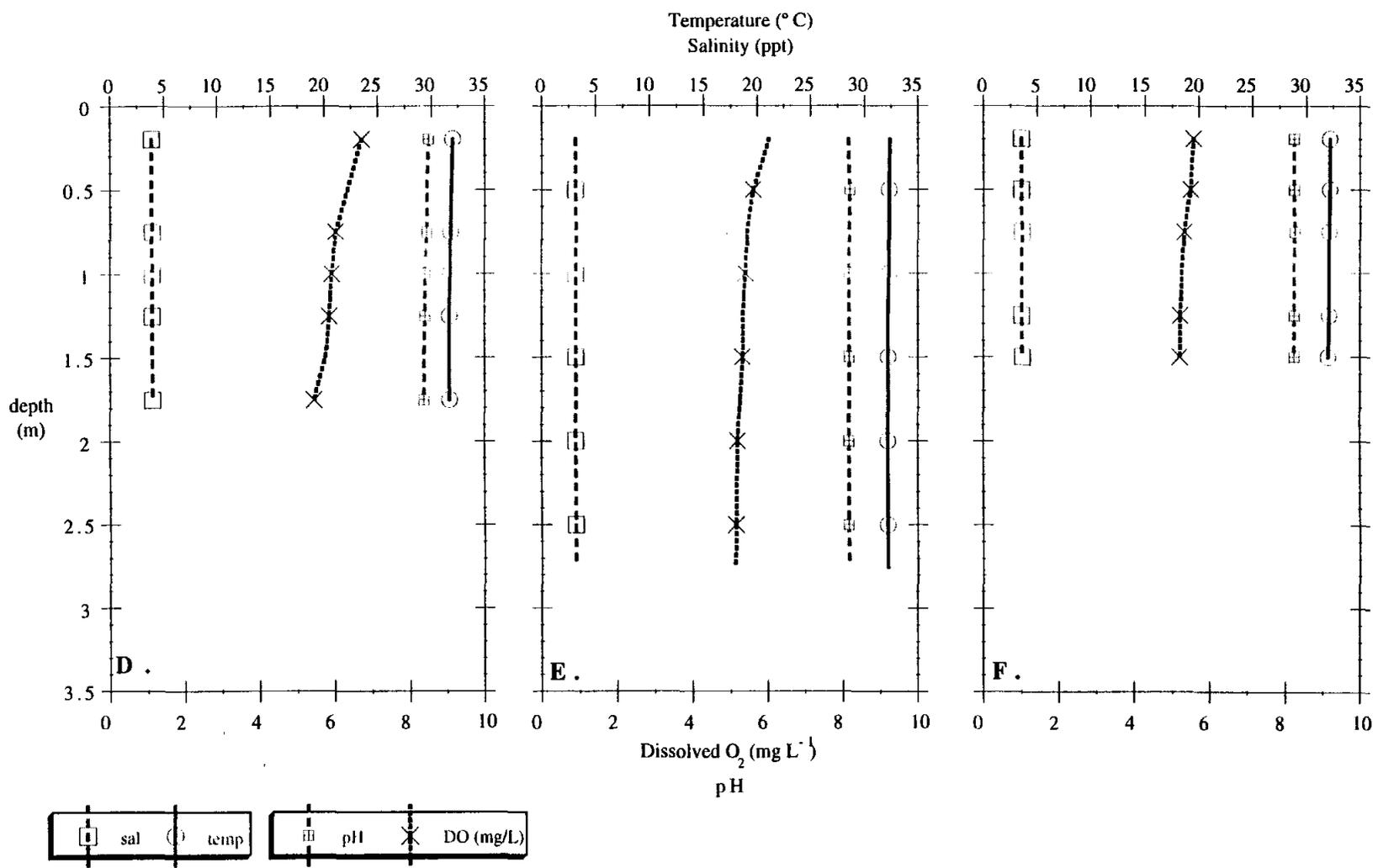
Temperature (° C)
Salinity (ppt)

Figure 2: Depth profiles of temperature (O) and salinity (□) [upper axis] and dissolved O_2 (×) 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.

Temperature (° C)
Salinity (ppt)

depth (m)

Dissolved O$_2$ (mg L^{-1})

pH

sal   temp   pH   DO (mg/L)

D.   E.   F.

- 17 -

Temperature (° C)
Salinity (ppt)

depth
(m)

G .

H .

I .

Dissolved O₂ (mg L⁻¹)

p H

| sal | temp | pH | DO (mg/L) |

Temperature (° C)
Salinity (ppt)

depth
(m)

J.

K.

Dissolved O₂ (mg L⁻¹)

pH

sal   temp   pH   DO (mg/L)

Figure 3: Depth profiles of salinity (A, B) and dissolved O_2 (C, D) along Trinity River salinity gradient stations in August 1998. Station identifications are provided in the figure legend.
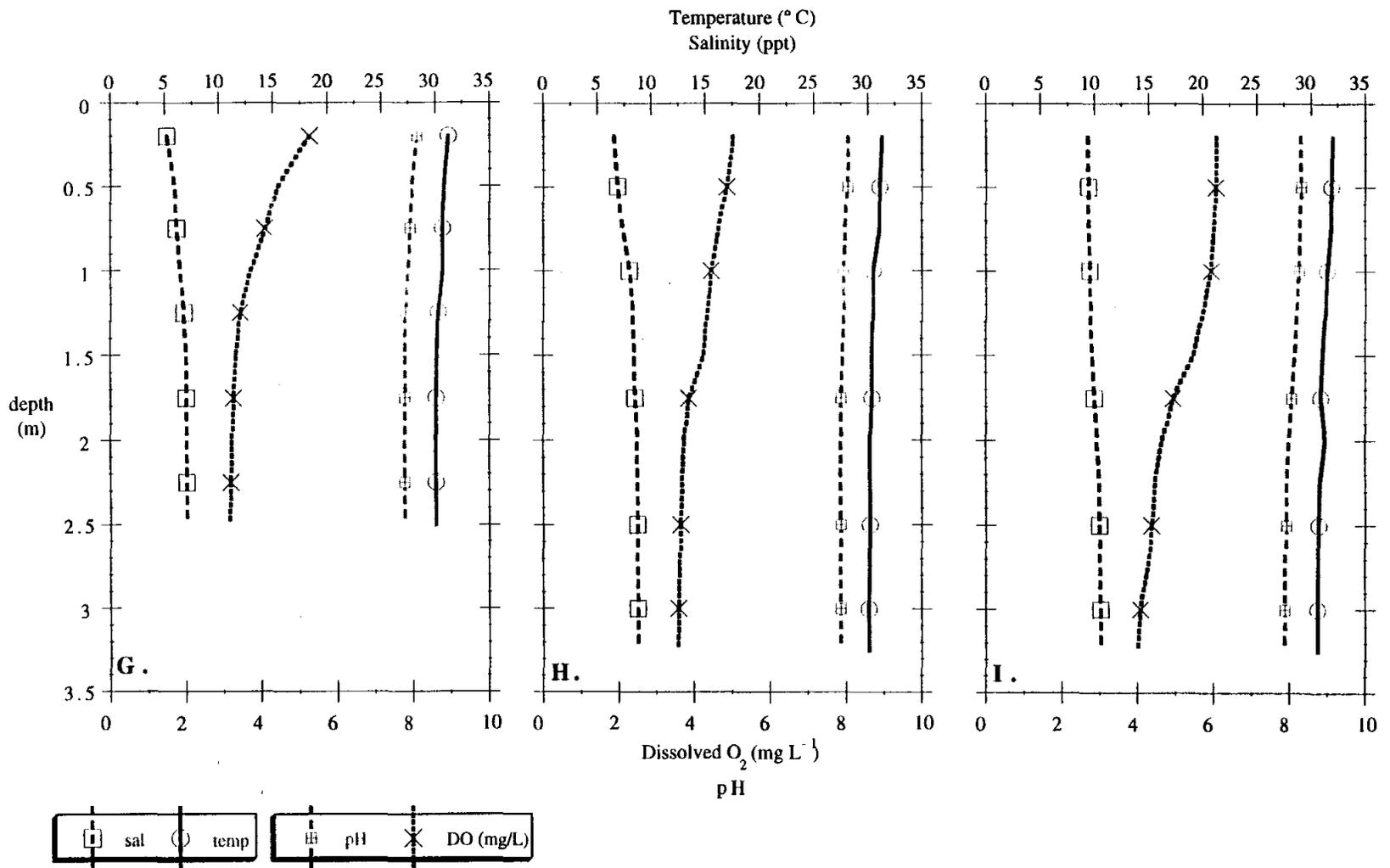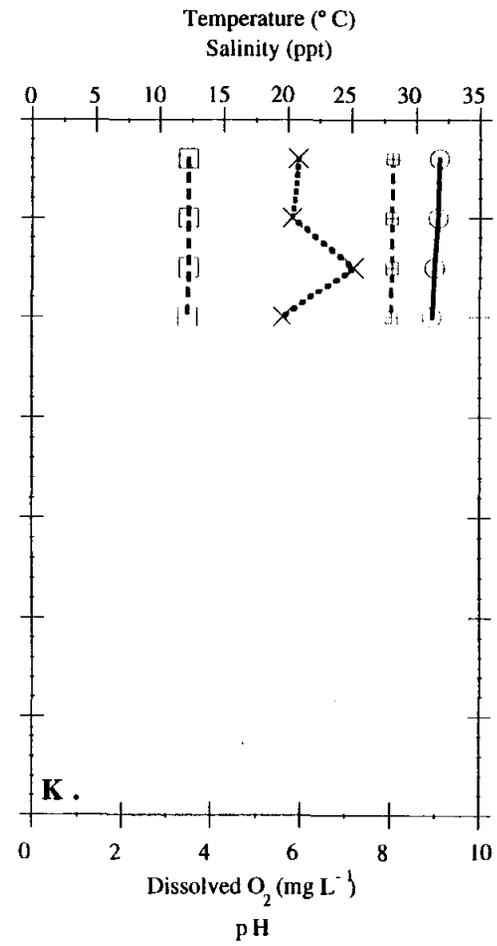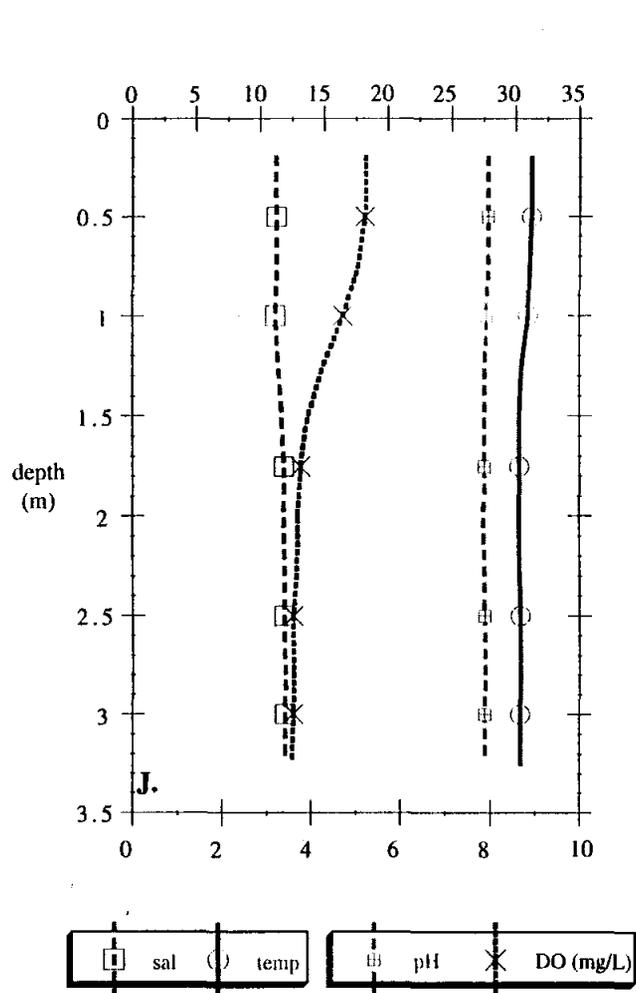
Figure 4: Depth profiles of temperature (O) and salinity (☐) [upper axis] and dissolved O_2 (×) and pH (□) [lower axis] during November 1998. Stations are listed as follows: A: Texas City; C: East Bay; D: Sta. 1; E: TR 1; F: TR 2; G: Sta. 2; H: TR 3; I: TR 4; J: Sta. 3; K: Sta. 4; L: Sta. 5. Symbols are consistent on panels A-L.

Temperature (° C)
Salinity (ppt)

depth (m)

Dissolved O₂ (mg L⁻¹)

pH

sal   temp   pH   DO (mg/L)

Temperature (° C)
Salinity (ppt)

depth (m)

Dissolved O$_2$ (mg L^{-1})
pH

sal   temp   pH   DO (mg/L)

G.   H.   I.

Temperature (° C)
Salinity (ppt)

depth
(m)

J.

K.

L.

Dissolved O$_2$ (mg L^{-1})

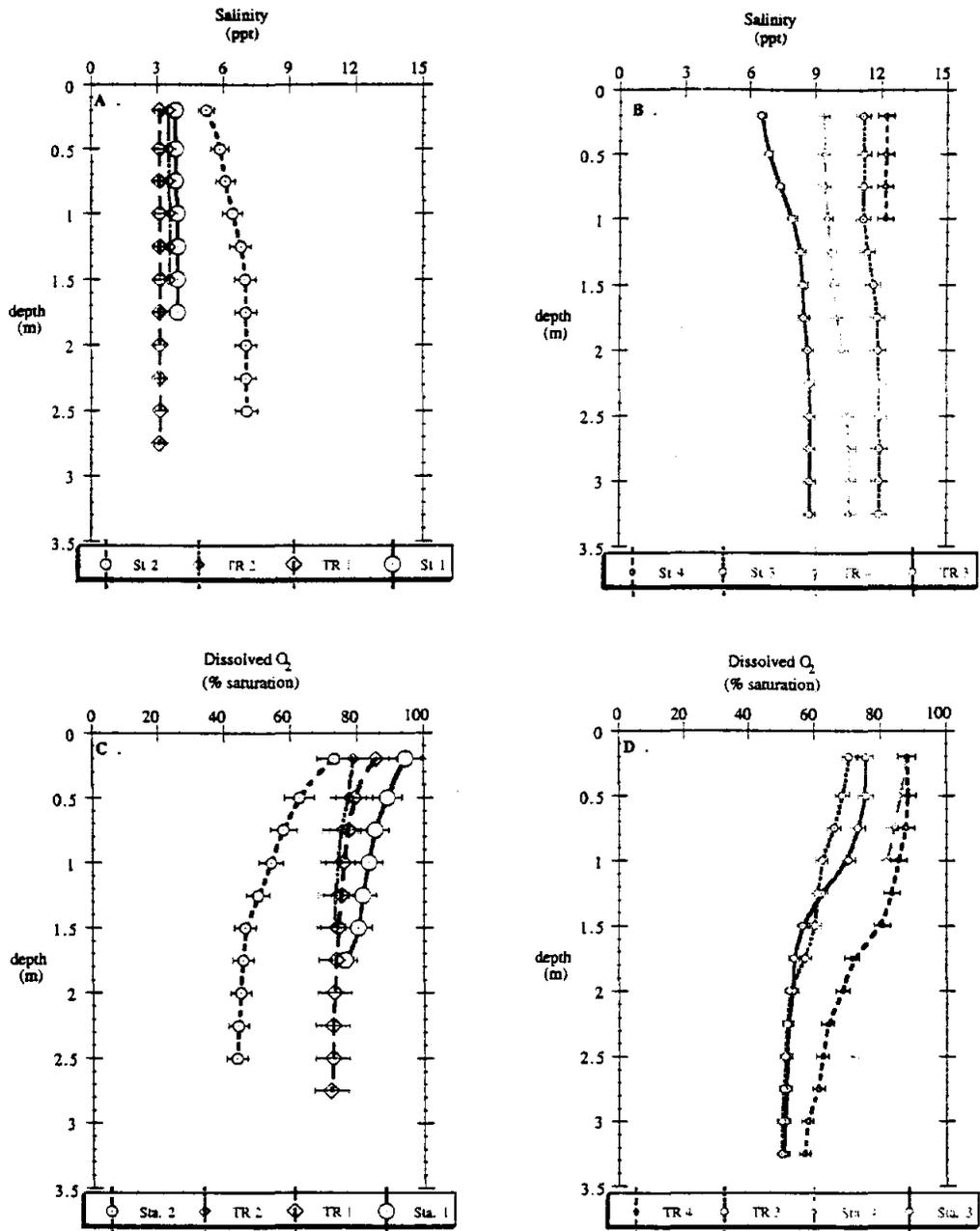pH

| | sal | | temp | | | pH | | DO (mg/L) |

Figure 5: Depth profiles of salinity (A, B) and dissolved O_2 (C, D) along
Trinity River salinity gradient stations in November 1998. Station
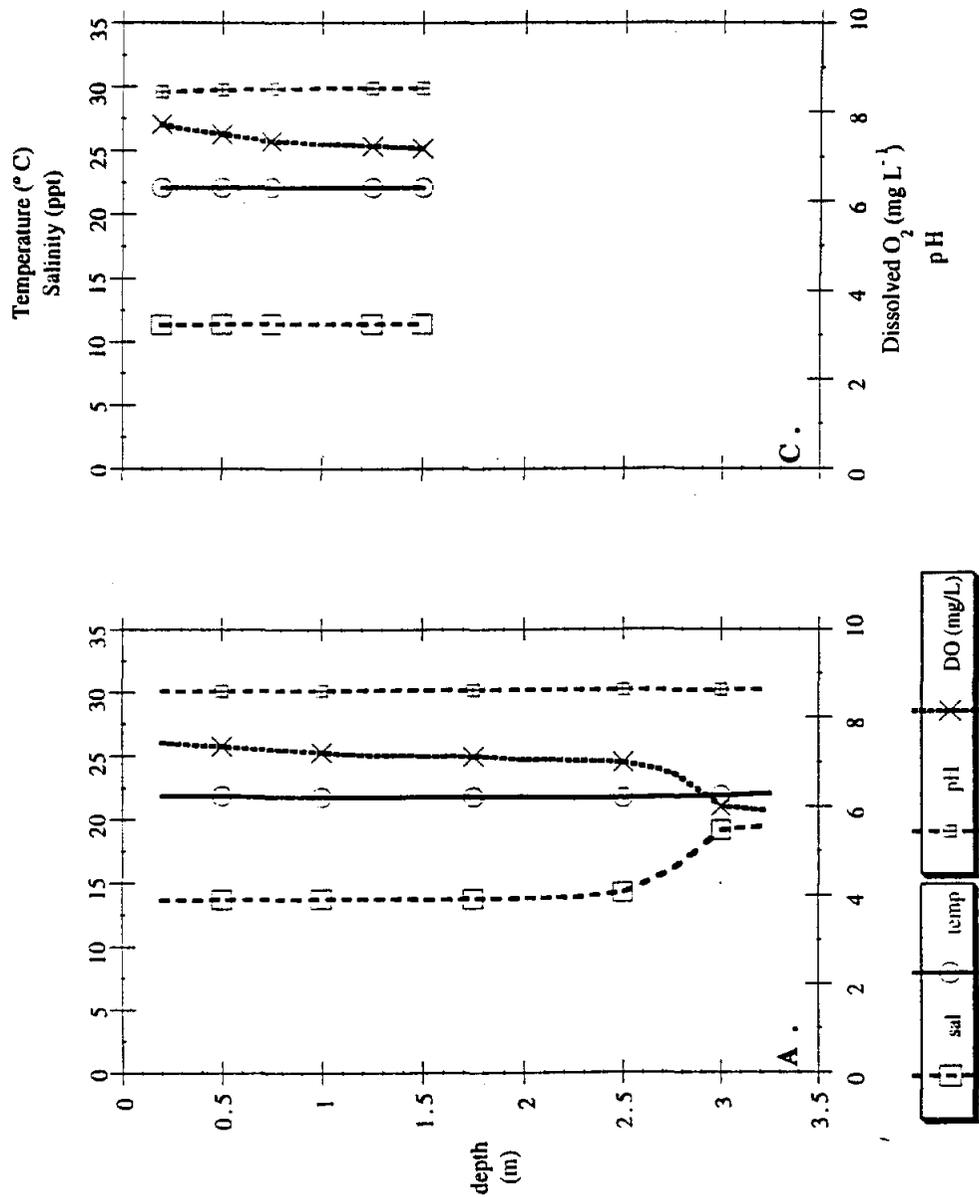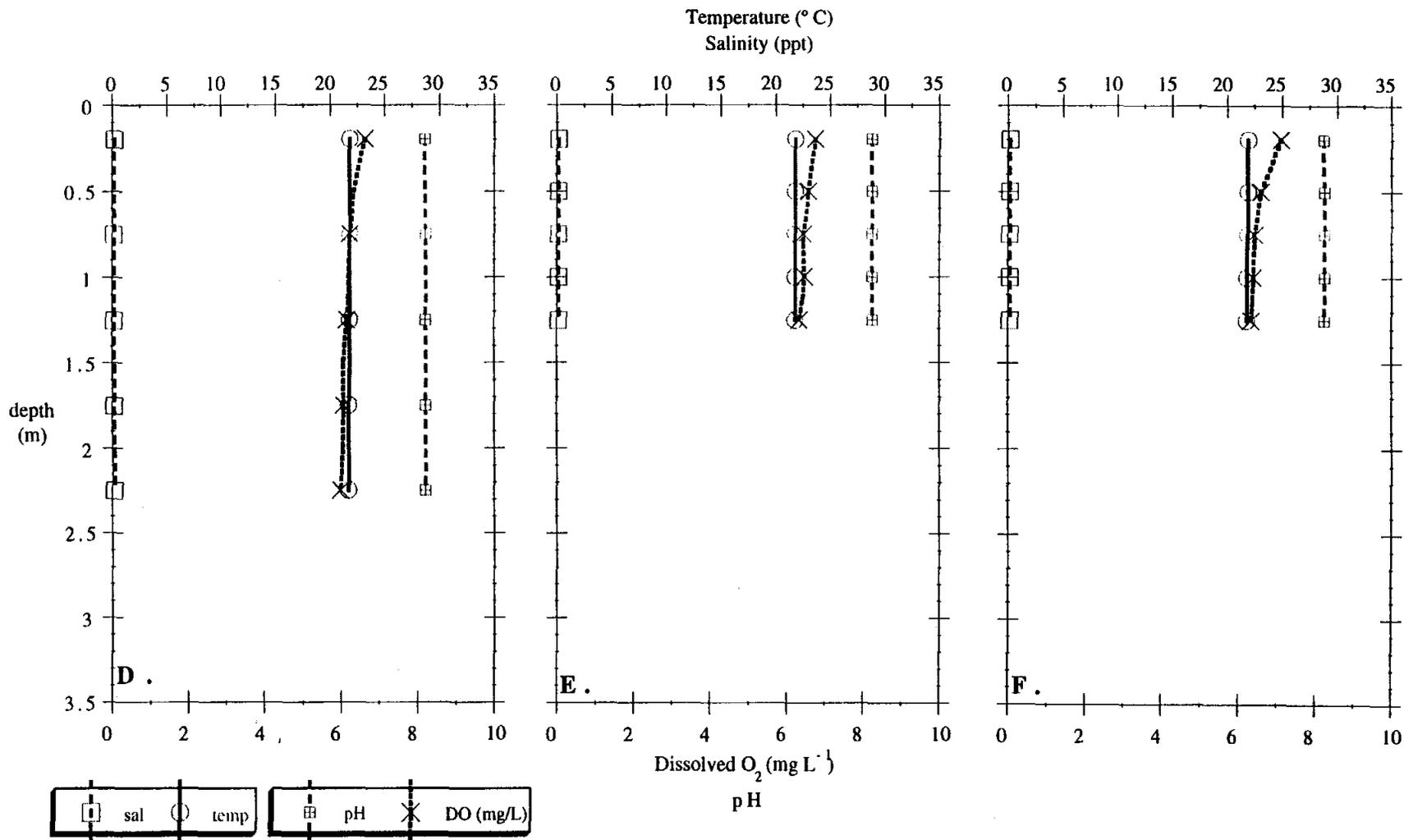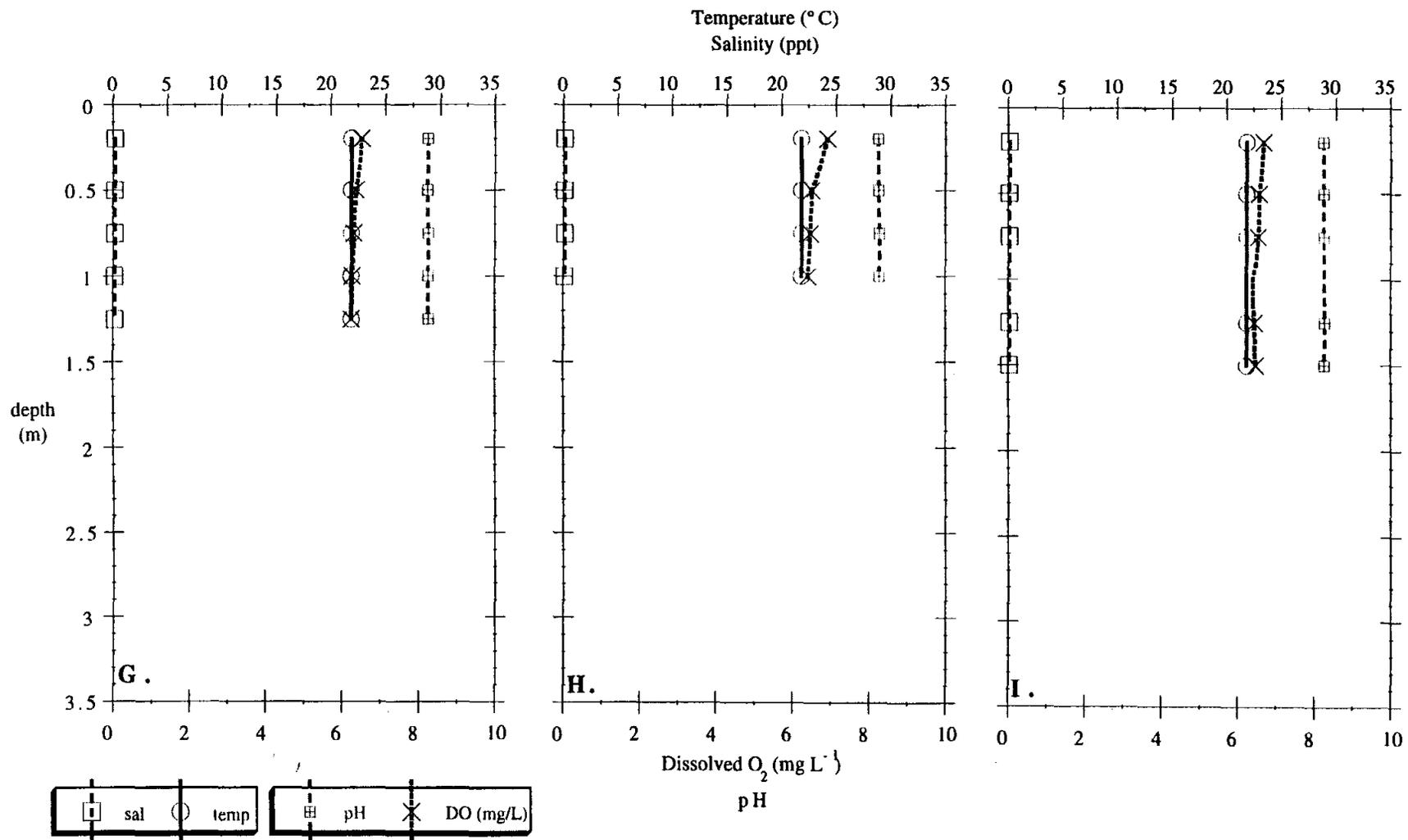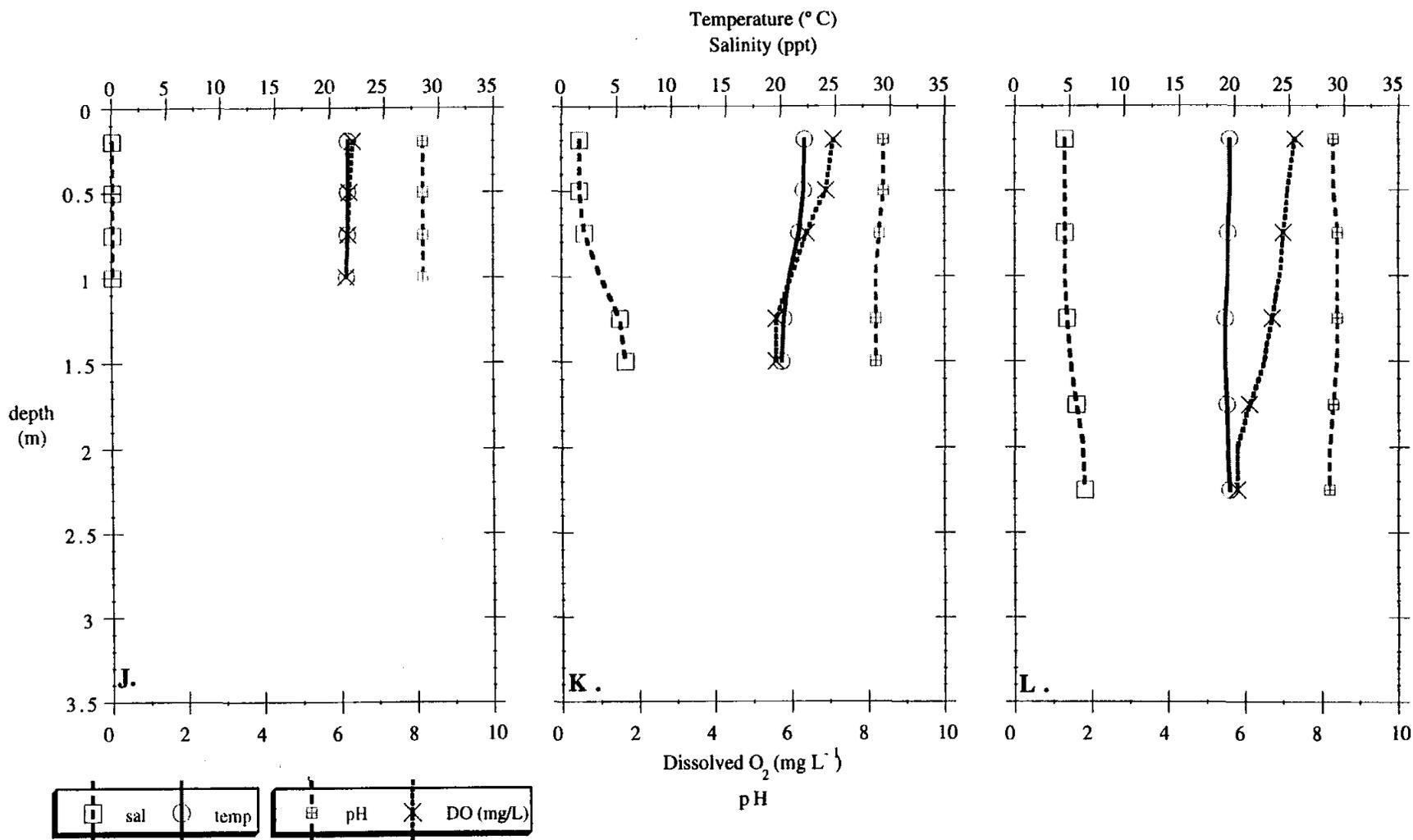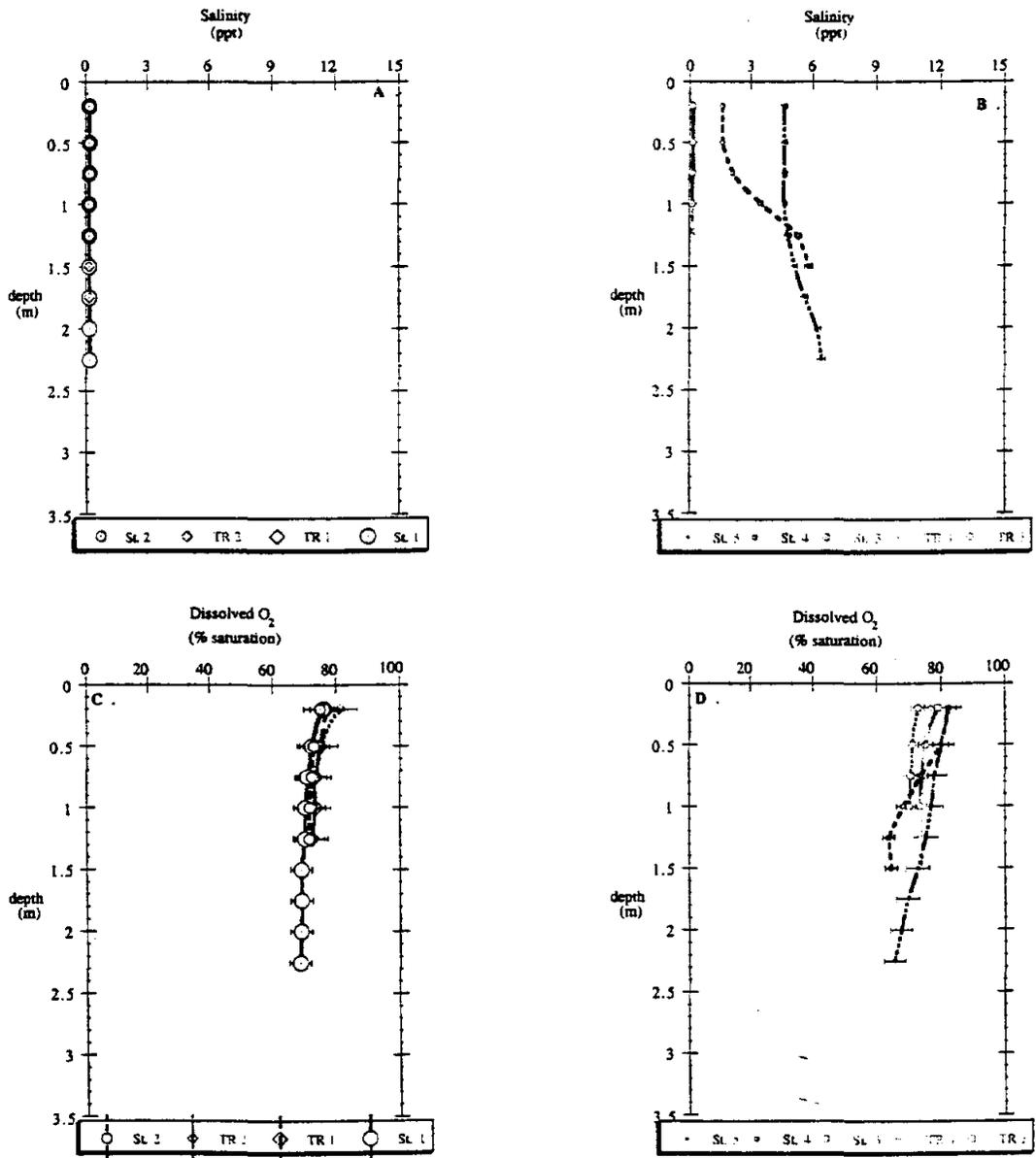identifications are provided in the figure legend.

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 dissoved O_2. Dissolved O_2 % 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_2 % saturation varied between 60 and 80 % in the more saline stations (St. 4 and 5) (Fig. 5). As mentioned previously, dissolved O_2 % 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_2 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_2 concentration were observed in August 1998 (Fig. 7A). The lowest dissolved O_2 concentration were observed at St. 2, TR 3 and TR 4; these surface to bottom changes reflected a 40% decrease in dissolved O_2 inventory over a 2 m water column (Fig. 7B). Twenty percent reductions in dissolved O_2 concentration were observed at Stations 4 and 5 in October of 1998 (Fig. 7B). The high O_2 demand apparent from these O_2 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 mg O_2 L^{-1}) conditions. Marked affects on water column nutrient distributions were observed (see below). This pattern suggests that
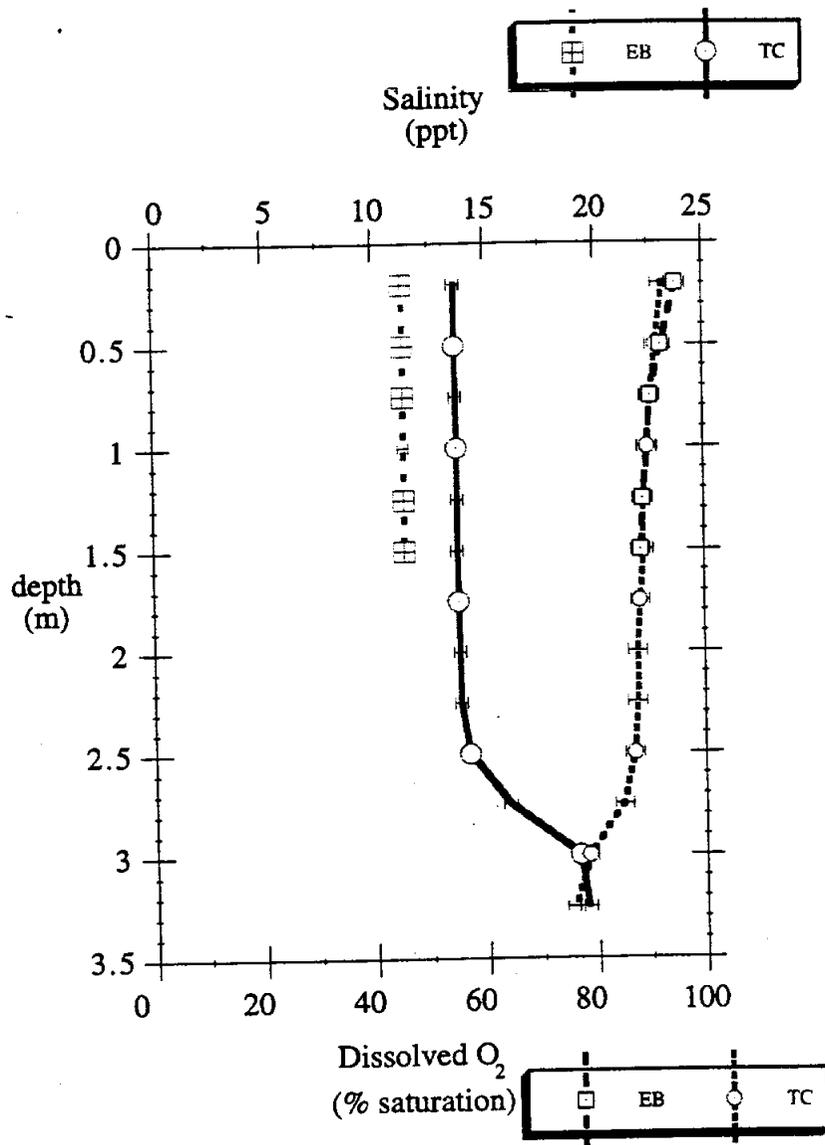
Figure 6: Depth profiles of salinity (upper axis) and dissolved O_2 (lower axis) at Texas City and East Bay stations in November 1998. Station identifications are provided in the figure legend.
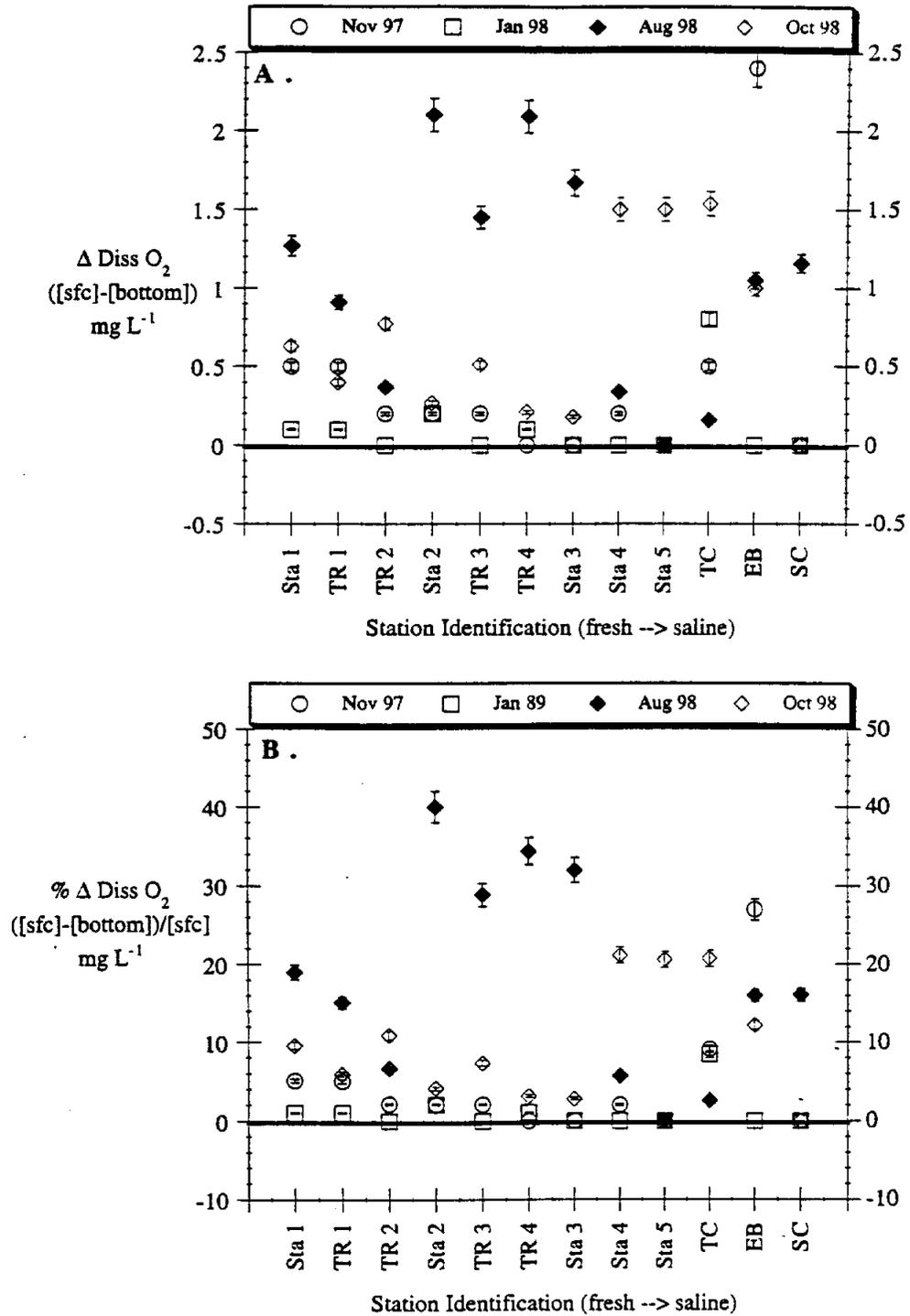
Figure 7: Difference in dissolved O_2 concentration over depth at all stations (X axis) between Nov. 1997 and Oct. 1998. Panel (A) illustrates the difference in concentration (mg L^{-1}) between surface and bottom stations (i.e., surface concentration – bottom concentration). Panel (B) illustrates the 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 industial exports or from a natural drought, will have deleterious affects 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 an 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_2 depletion of bottom waters. Furthermore, when low O_2 water overlies a sediment, ammonium and phosphorus remineralization are stimulated. The lack of O_2 limits coupled nitrification-denitrification, which increases net N regeneration rates. Low O_2 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_2 conditions also increase mobilization rates of heavy metals (Cu, Zn). Additional negative impacts of low O_2 conditions in river water include reductions in biomass of sediment infauna (many invertebrates cannot tolerate low O_2 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

(NH_4), nitrate (NO_3) and phosphate (PO_4) were low (1-6 μM) and similar

between surface and bottom waters. Nitrite (NO_2) concentration was always low

(< 0.5 μM) and invariable from St. 1 to 4. NH_4 and PO_4 concentration increased

slightly between St. 1 and 4 while NO_3 concentration varied between stations.

Lower 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), NO_3

concentration in surface and bottom waters are elevated (Fig. 8 C – F, G & H).

NO_3 is the dominant inorganic nutrient form during high flow periods, being

almost 10 times more abundant than NH_4, NO_2 and PO_4. Phosphate

concentrations are ~ 1-2 μM during periods of high flow. Uptake of NO_3 and

production of NH_4 are apparent at higher salinity stations even during high flow

(Fig. 8 E, F). During August of 1998, water column 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 higest

NH_4 concentrations were observed at the Trinity mid-rivers stations, which

exhibited the lowest bottom water dissolved O_2 concentration (Fig. 7, Fig. 8 G,

H). 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 NO_3 concentrations, particularly at the freshwater sites (Fig. 8 I, J).

Uptake of NO_3 in bottom waters was apparent (bottom water concentration was

less than surface water conc.) in freshwater stations while bottom waters NO_3

production was suggested at Sta. 5 (Fig. 8 I, J). 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

PO_4 concentration was highest at Sta. 5, possibly resulting from high rates of

benthic metabolism and release of 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
	Nov-97								
St 1 ·		1.50	0.18	3.90	1.10	3.24	0.34	4.30	1.48
St 3		3.06	0.29	3.40	2.06	3.60	0.14	5.56	2.22
St 4		4.50	0.11	6.29	3.96	5.31	0.16	3.50	2.61
NO DATA FOR TRANSEC STATIONS IN NOV. 1997									
	Jan-98								
TC		0.00	1.38	22.73	0.88	0.00	0.93	18.93	1.23
St 1		0.09	1.08	48.35	0.15	0.00	n. d.	n. d.	n. d.
St 2		0.51	1.16	46.16	0.10	0.00	1.14	46.41	0.13
St 3		0.00	0.92	36.03	0.10	0.05	0.91	34.23	0.15
St 4		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
	Apr-98								
TC		3.37	0.849	6.30	0.70	4.75	0.44	2.60	1.55
EB		2.20	0.674	1.63	0.75	7.82	0.83	21.56	0.00
St 1		4.18	0.808	45.66	2.20	0.00	0.45	43.99	1.81
St 2		1.18	0.636	45.03	1.83	0.00	0.581	44.75	1.74
St 3		2.27	0.683	43.43	2.01	1.60	0.37	44.55	1.30
St 4		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
	Aug-98								
TC		1.27	0.26	0.00	0.31	3.00	0.80	1.25	0.00
EB		3.98	0.36	0.00	1.61	13.00	0.38	0.40	1.70
SC		0.99	0.32	0.00	2.39	1.15	0.60	1.55	1.30
St 1		1.91	0.33	0.00	1.14	2.00	0.35	0.00	1.20
St 2		2.99	0.34	0.09	0.90	15.85	0.47	0.50	1.02
St 3		5.52	0.40	0.00	1.20	2.12	0.49	0.45	1.47
St 4		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
	Oct-98								
TC		0.00	6.70	13.55	5.56	1.86	4.80	11.91	2.83
EB		0.00	6.38	13.08	1.98	1.74	7.10	15.90	2.80
St 1		5.25	0.58	9.86	1.40	4.13	0.55	10.70	0.90
St 2		2.06	0.32	7.33	1.98	1.99	0.12	7.46	1.62
St 3		4.14	0.91	9.76	4.36	7.89	0.65	10.20	1.55
St 4		8.92	1.35	9.82	2.91	16.10	2.60 `	10.30	3.50
ST 5		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
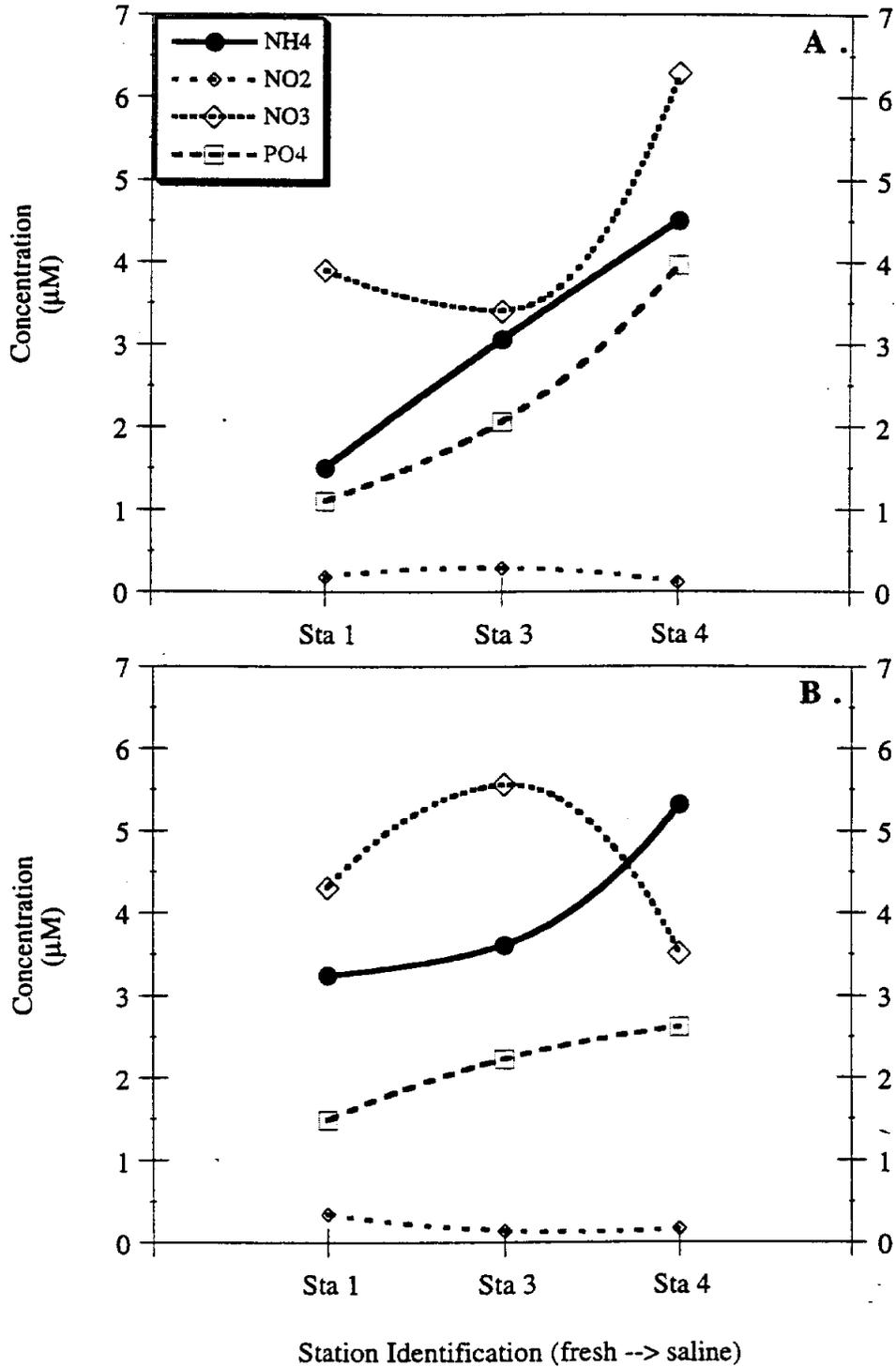
Figure 8: Surface and bottom concentration of ammonium (●), nitrite (◇), nitrate (◇), and phosphate (□) in November 1997 (A, B); January 1998 (C, D); April 1998 (E, F); August 1998 (G, H); and November 1998 (I, J). The x-axis is station location, progressing from fresh to saline stations.

Concentration (μM)

Concentration (μM)

Station Identification (fresh --> saline)

St 1 TR 1 TR 2 St 2 TR 3 TR 4 St 3 St 4 ST 5 TC EB

I.

J.

NH4 NO2 NO3 PO4

- 36 -
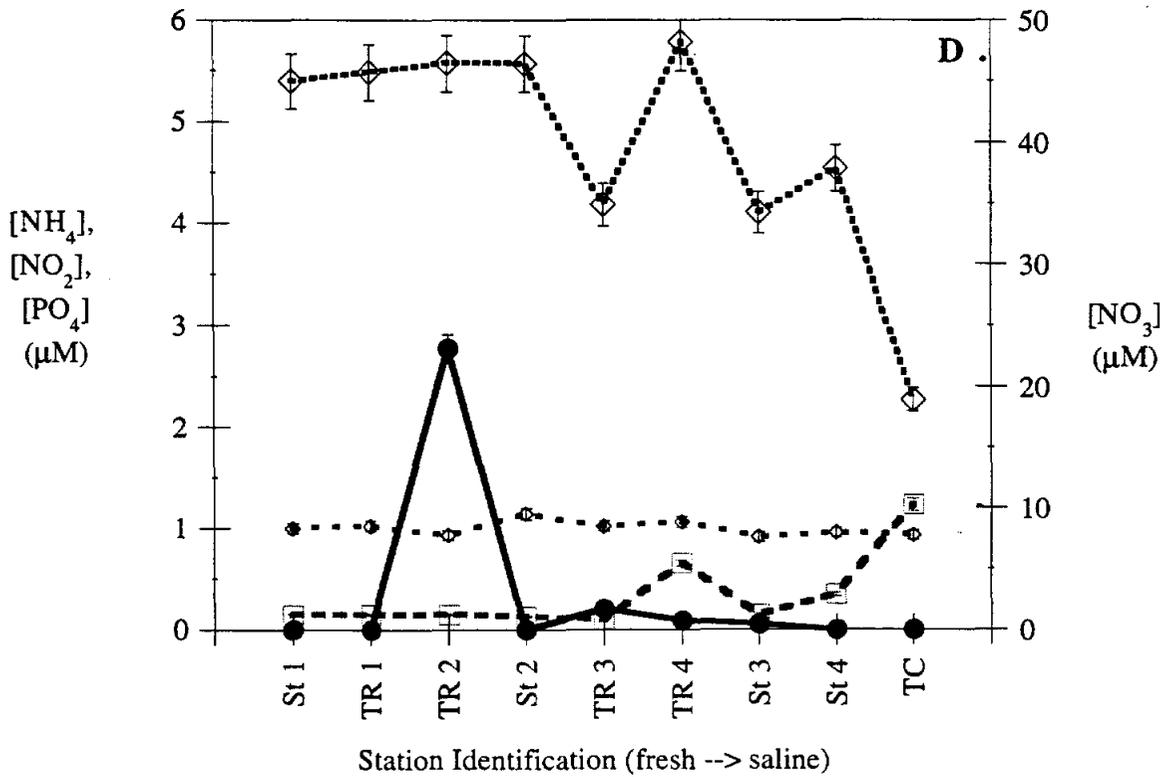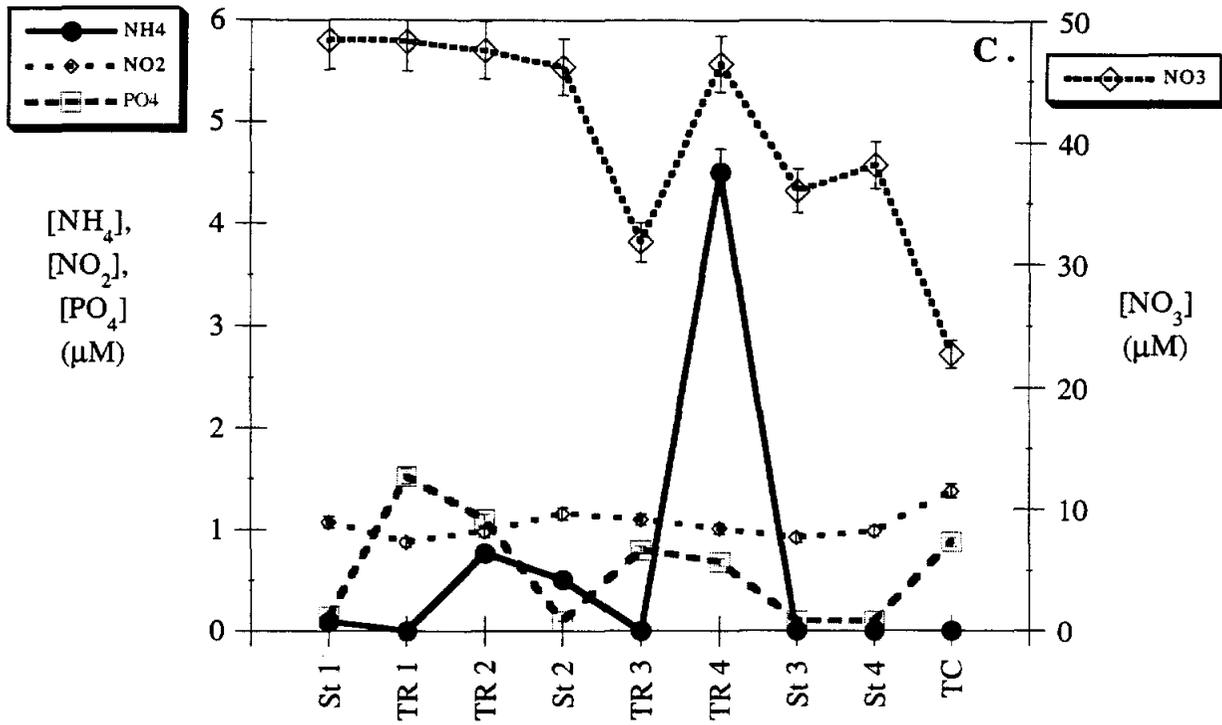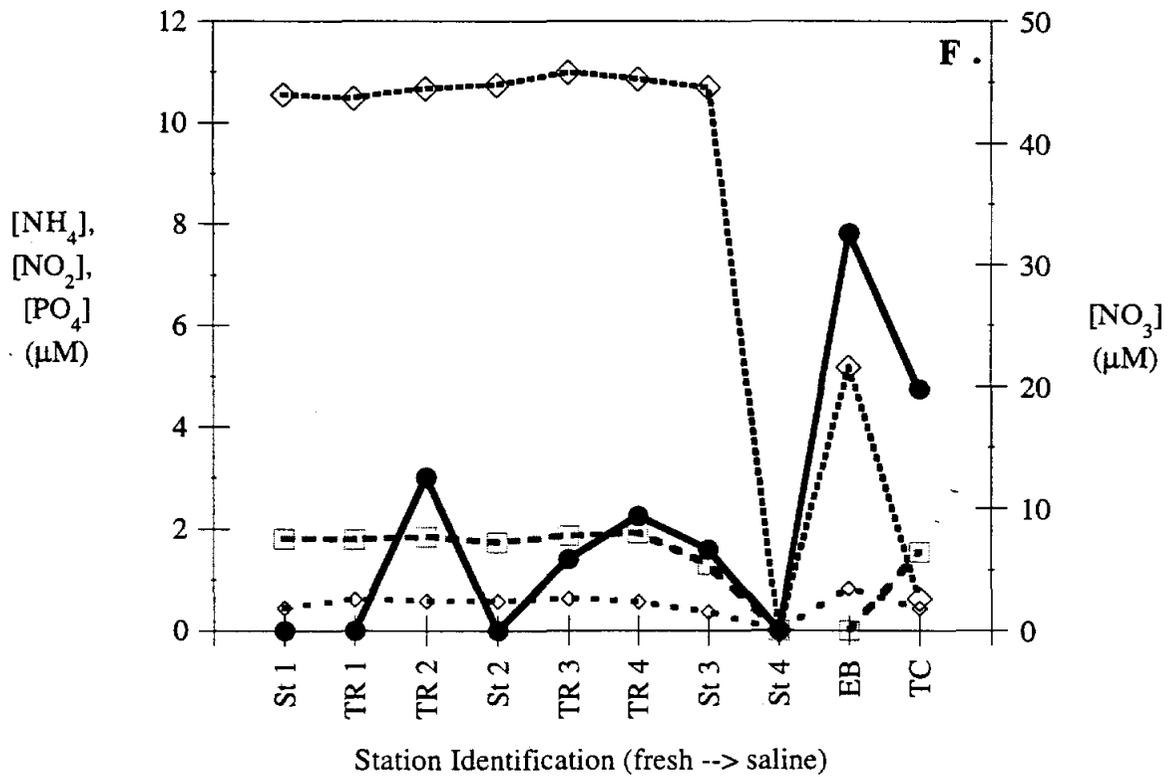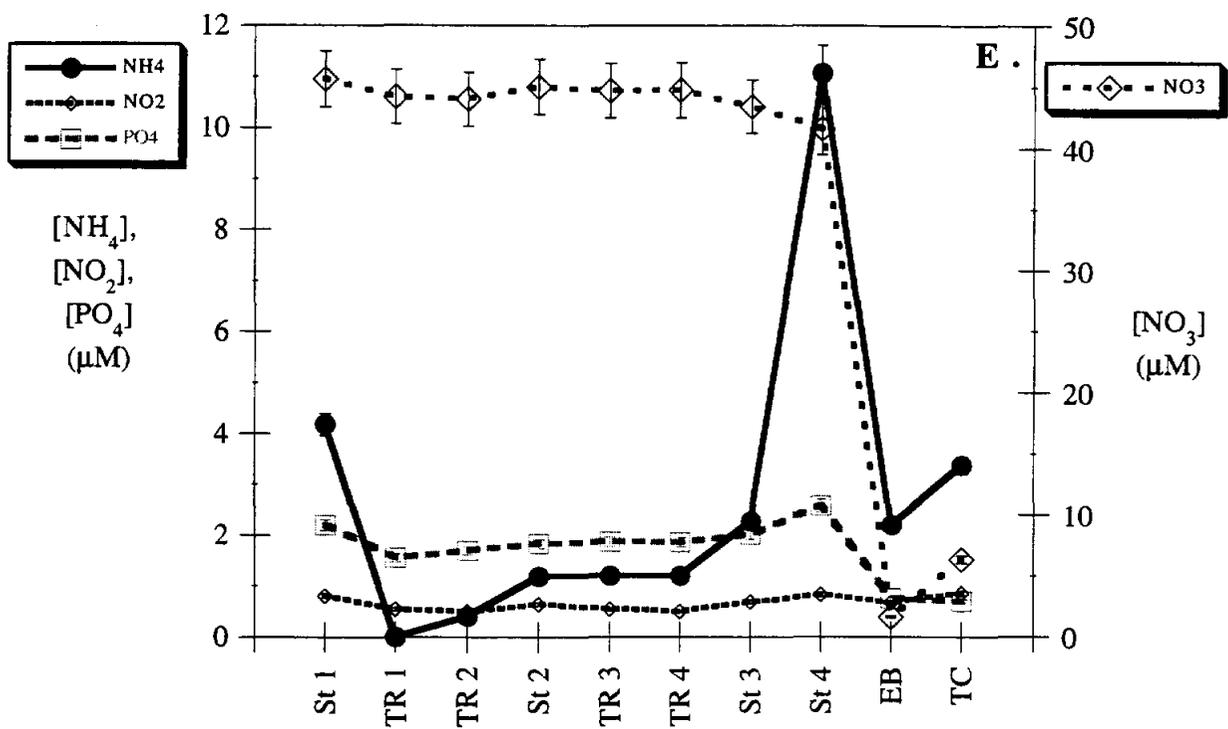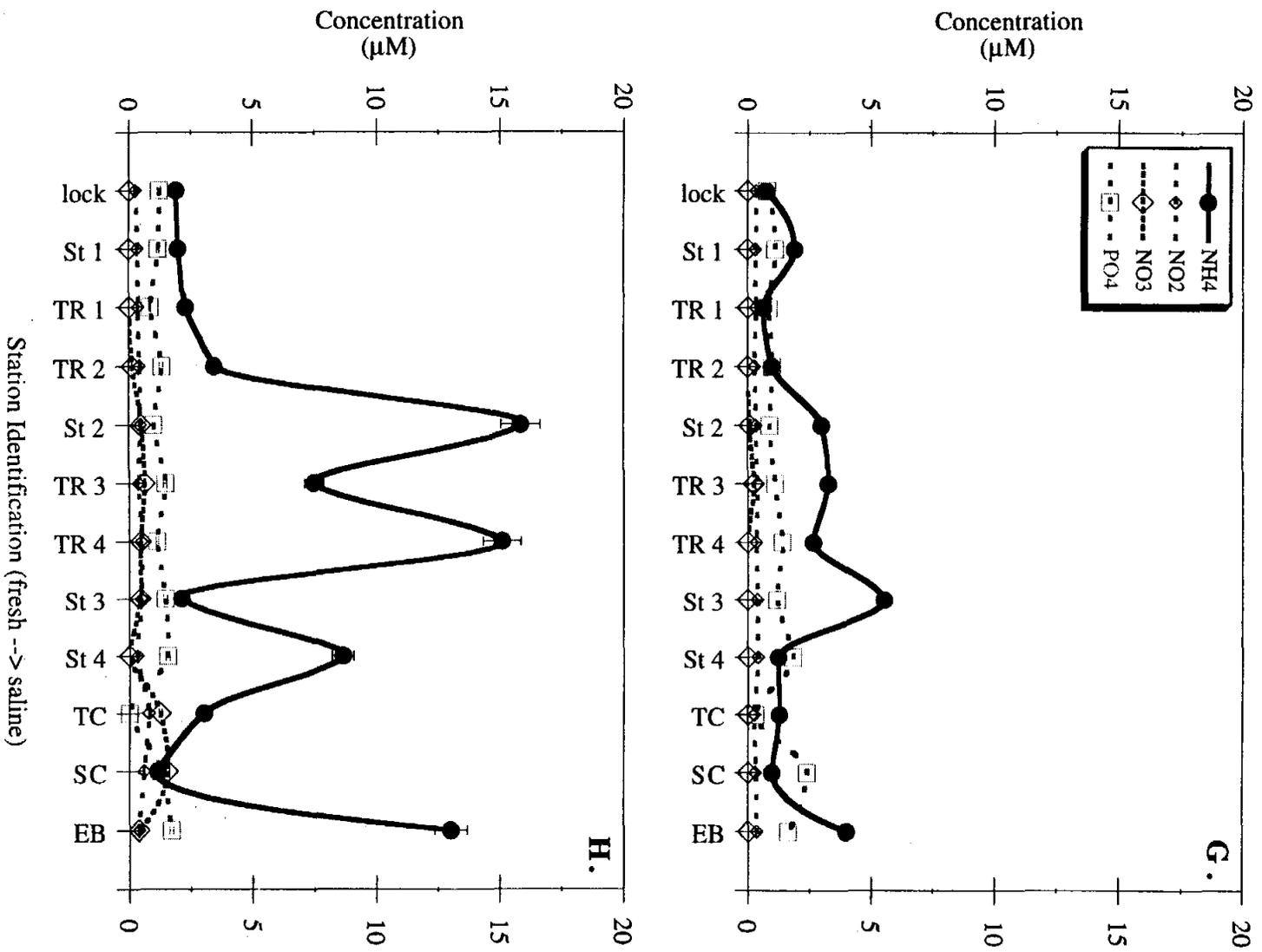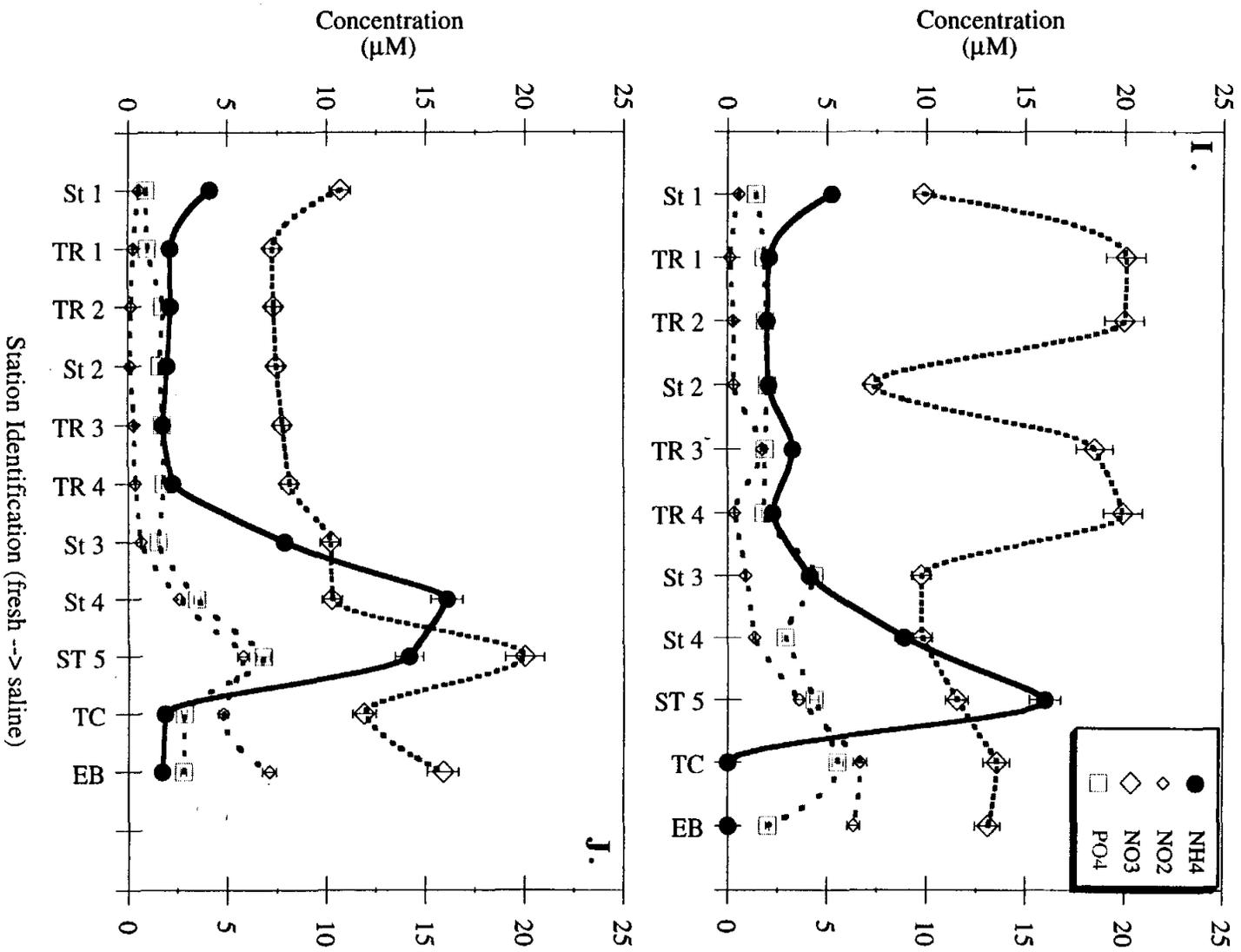
Surface water NH_4 concentrations were higher during 1998 than observed during the previous years of this study (Table 2, Joye and An 1998), with maximal values (16 μM) being ~ 4 times higher than maximal values observed previously (~ 4μM; Joye and An 1998). Bottom water ammonium concentrations were higher than those observed during 1997 (1 μM) but similar to those observed during 1996 (10 μM). Dissolved phosphate concentrations did not exhibit as much variability between 1996 and 1998. Average concentrations in surface waters were approximately 2-3 μM during 1996 and 1998 versus 1 μM during 1997.

Water column NO_3 was the dominant inorganic N form during high flow (e.g. January 1998) whereas NH_4 assumed that role during low flow (e.g. August 1998). NO_3 concentrations during 1998 (45 - 50 μM) were higher than those observed during 1996 or 1997 (30 - 35 μM). 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 ~ 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 – 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 ~ P limitation) and excess DIP present during low flow (summer ~ N limitation).

Pore water nutrient concentrations. Pore water concentrations in sediment cores collected between November 1997 and October 1998 are shown in Figures 9 though 13. Pore water NH_4, nitrate + nitrite (NO_x) and 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 NH_4 concentration ranged from 450 μM at depth in St. 1 sediments to 1500 μM at depth in St. 3 and 4 sediments (Fig. 9). 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 PO_4 concentrations were almost always low (< 2 μM). This probably results from the binding of 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 NH_4 and production of NO_x was observed throughout the upper 5 to 10 cm of the sediment column. NO_x concentrations were similar to those observed in November and exhibited either a shallow (St. 4) or deep (St. 3) sub surface peak. PO_4 concentrations were higher (10 μM) than those observed during November and a pronounced PO_4 peak was apparent at 17 cm in the St. 4 core. This peak suggests a redox change, as 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 NH_4 and NO_x concentrations being similar.

During April 1998, concentration of NH_4 were similar to those observed during January, except at the Texas City site where concentrations were approximately 3-fold higher (Fig. 11). PO_4 concentration was between 2-6 μM at all sites while. Neither NH_4 nor NO_x exhibited the expected depth-dependent

Figure 9: Pore water concentrations of ammonium ($\blacklozenge$) [lower y axis] and nitrate+nitrite ($\bigcirc$) 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 (◆) [lower y axis] and nitrate+nitrite (○) and phosphate (□) [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 (O) 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.

NO$_3^-$ & PO$_4^{3-}$
μmol L^{-1}

NO$_3^-$ & PO$_4^{3-}$
μmol L^{-1}

NO$_3^-$ & PO$_4^{3-}$
μmol L^{-1}

E. Bay
4-98

Tx. City
4-98

Sh. Chan.
4-98

Depth
(cm)

NH$_4^+$
μmol L^{-1}

NH$_4^+$
μmol L^{-1}

NH$_4^+$
μmol L^{-1}

NH4

NO3

PO4

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. 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 NH_4 at St. 3 (Fig. 12). At the Texas City and Ship Channel stations, pore water NO_x concentrations were extremely high (>> bottom water concentration) throughout the upper 15 cm of the sediment column. NH_4 showed increased concentration with depth but concentrations were low (< 150 μM; Fig. 12). Despite higher 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 NO_x to pore waters. At St. 1, in particular, a deep (25 cm) peak in NO_x concentration (70 μM) was observed. We believe this deep peak reflects groundwater input to river sediments. At St. 3 and 4, the depth distribution patterns of NO_x and NH_4 were similar. As we have seen before, bioturbation results in erratic changes in pore water nutrient concentrations. At St. 5, NH_4 concentrations increase linearly with depth and PO_4 concentrations also increase. These are the highest PO_4 concentrations ever measured in Galveston Bay pore water (by us). The absence of NO_x at depth and the clear pattern of NH_4 and 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).
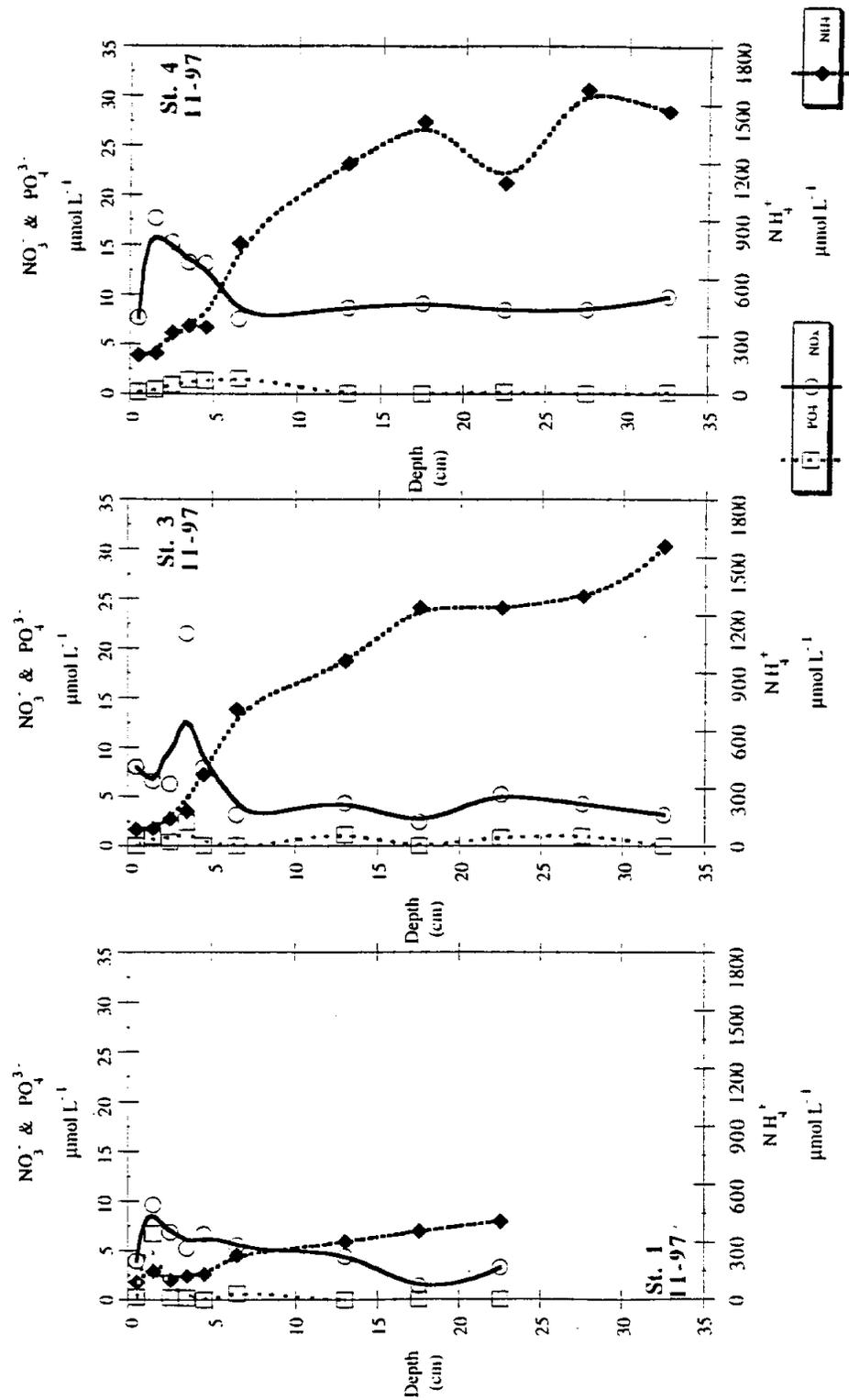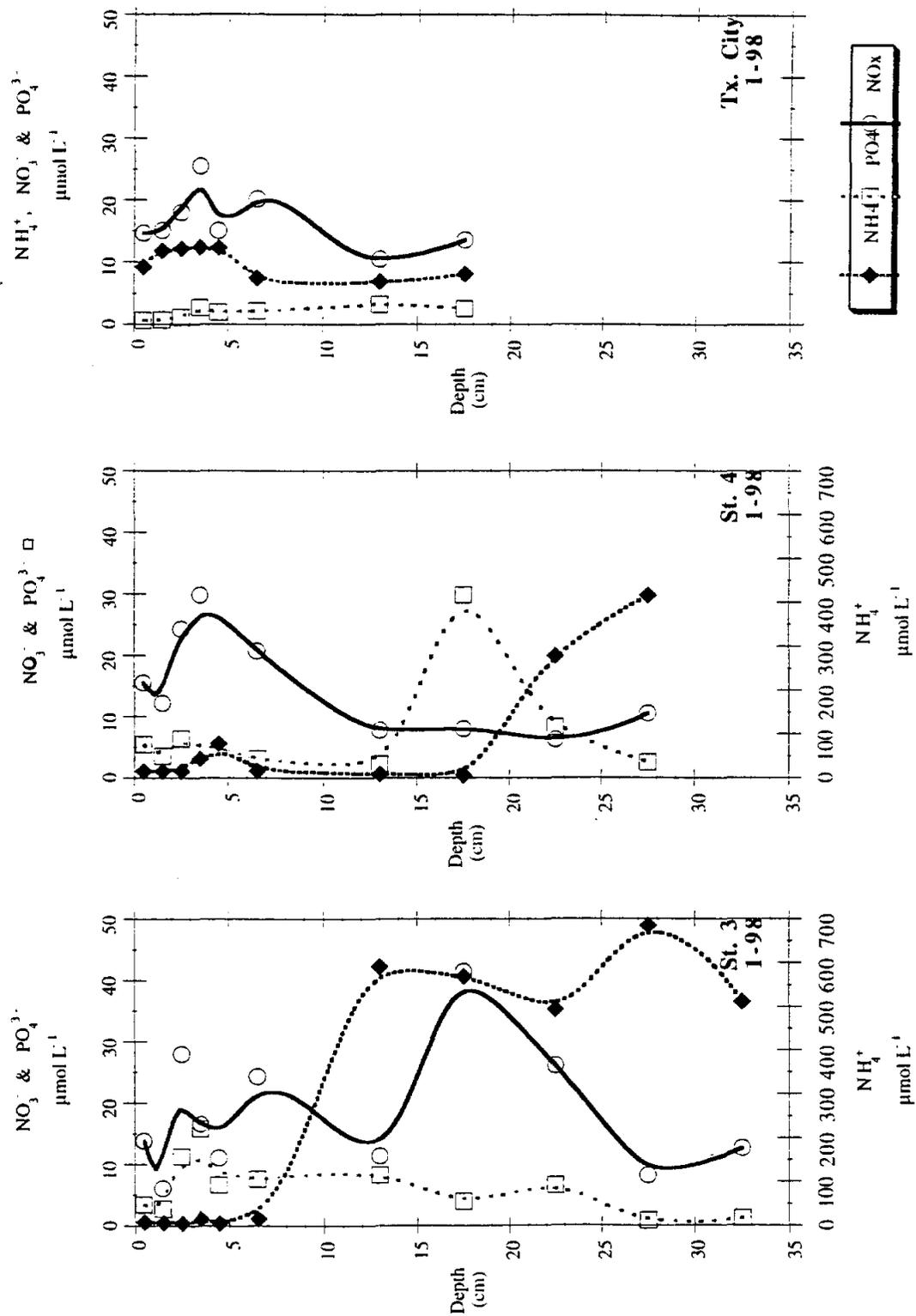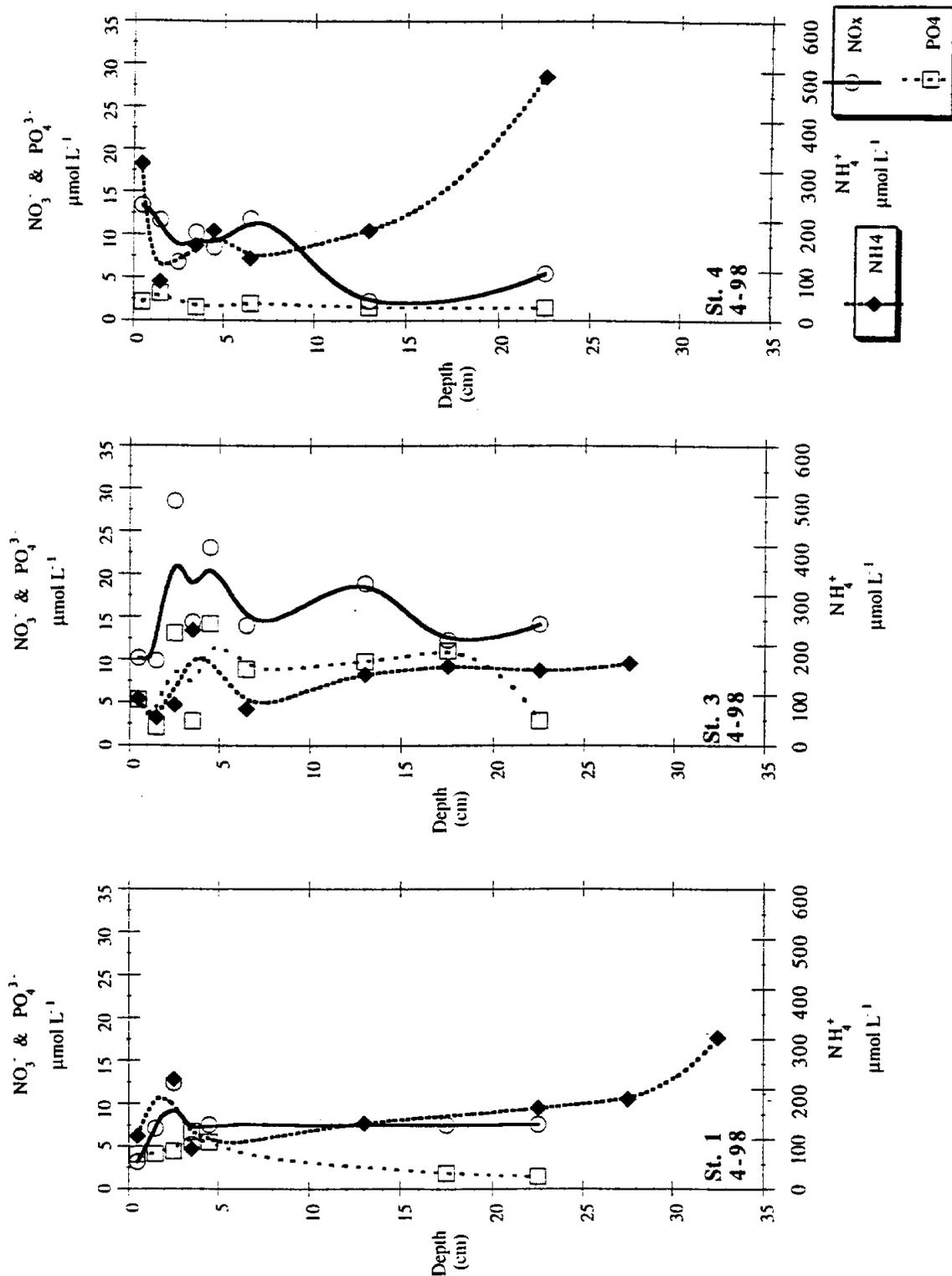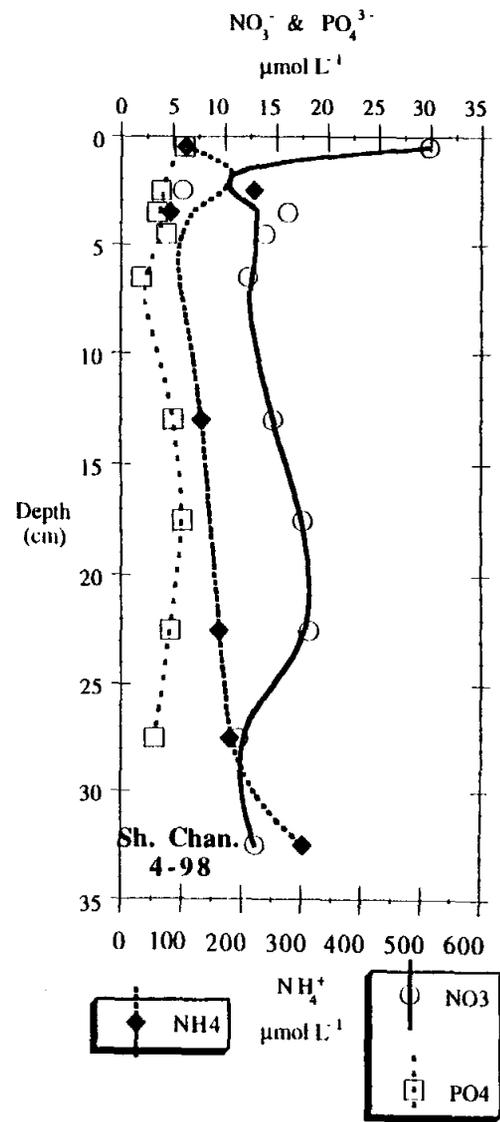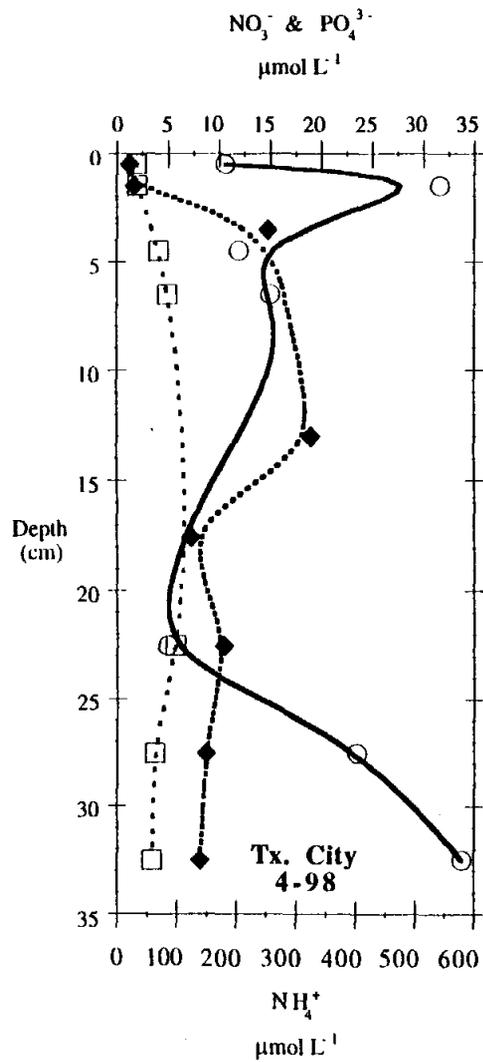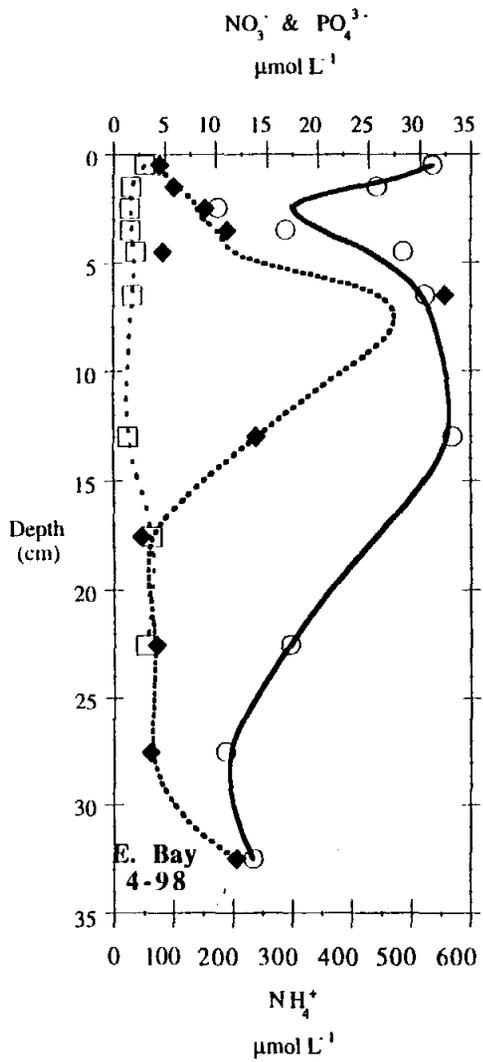
Figure 12: Pore water concentrations of ammonium (◆) [lower y axis] and nitrate+nitrite (O) and phosphate (□) [upper x axis] at Sta. 1, 3, 4, Texas City, East Bay and Ship Channel sites in August of 1998. Note that the scales of the two y-axes are different.

NO_3^- & PO_4^{3-}

$\mu mol\ L^{-1}$

0   5   10   15   20   25   30   35

Depth (cm)

0   300   600   900   1200   1500   1800

NH_4^+

$\mu mol\ L^{-1}$

TC
898

NO_3^- & PO_4^{3-}

$\mu mol\ L^{-1}$

0   5   10   15   20   25   30   35

Sh. Ch.
898

Depth (cm)

0   300   600   900   1200   1500   1800

NH_4^+

$\mu mol\ L^{-1}$

NO_3^- & PO_4^{3-}

$\mu mol\ L^{-1}$

0   5   10   15   20   25   30   35

Depth (cm)

EB
898

0   300   600   900   1200   1500   1800

NH_4^+

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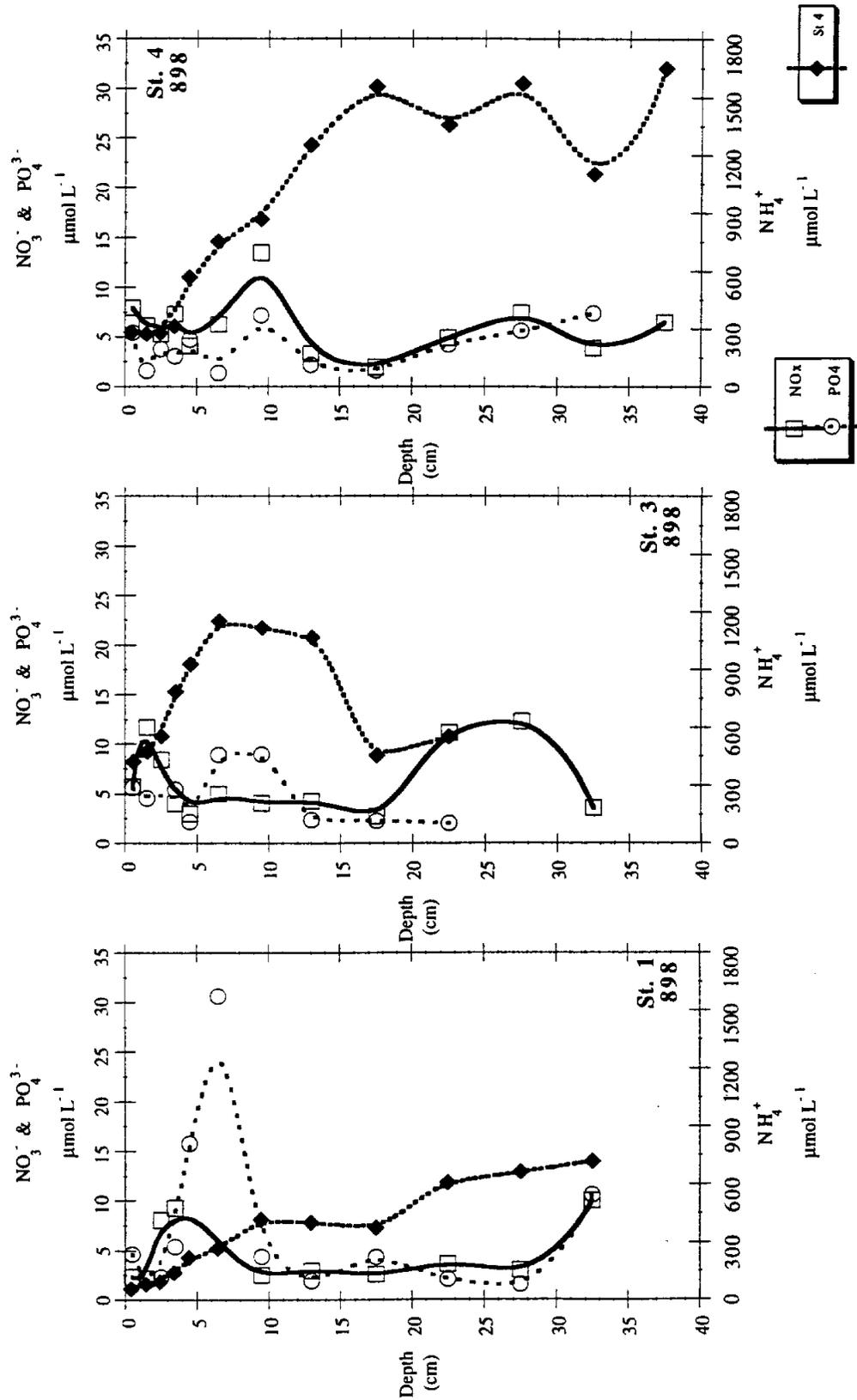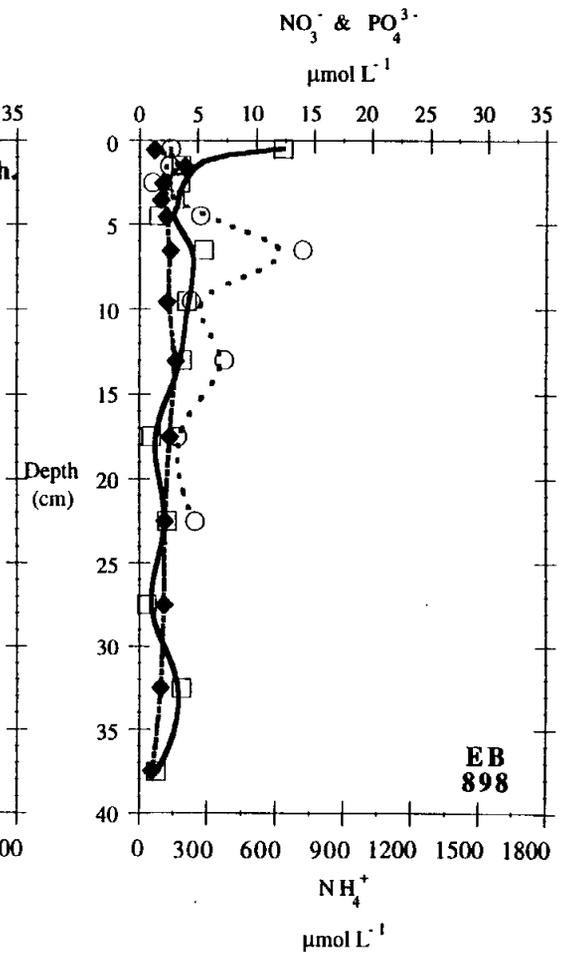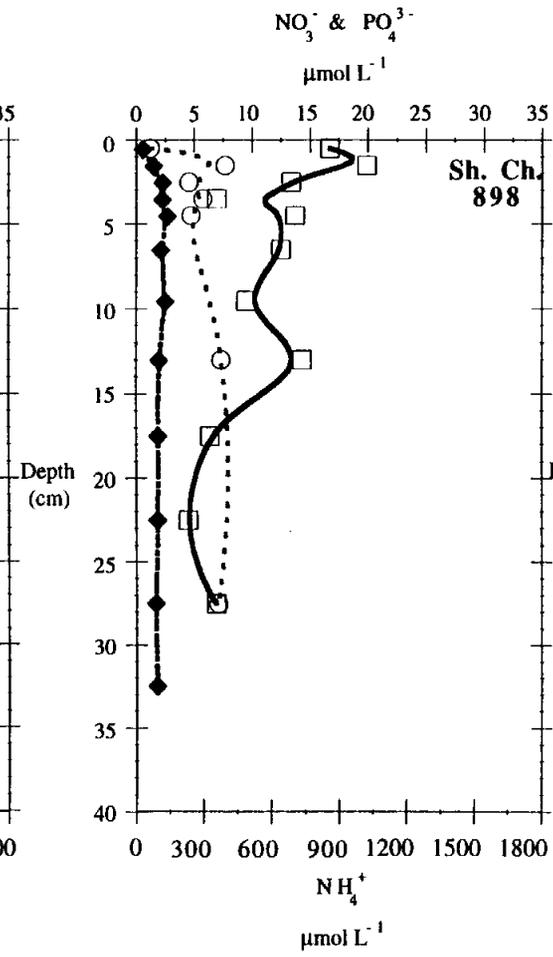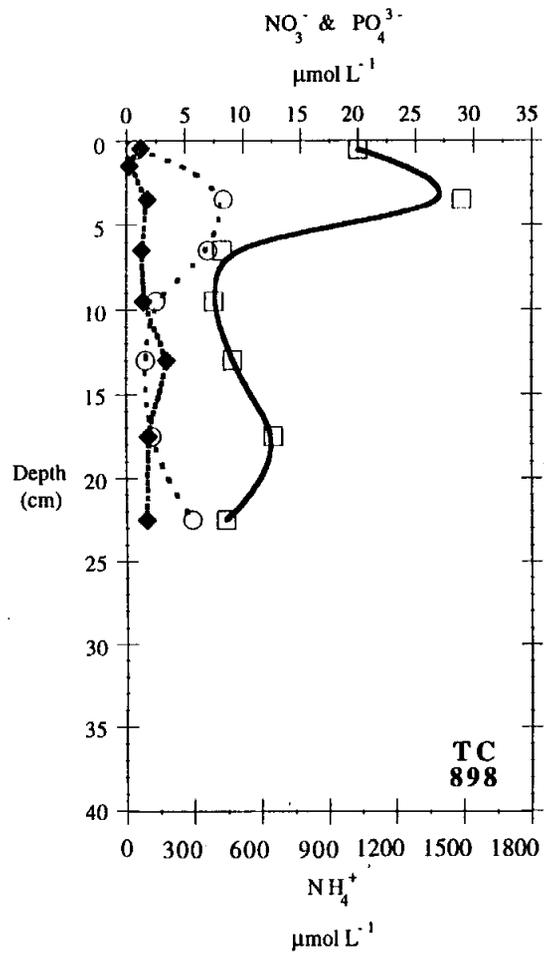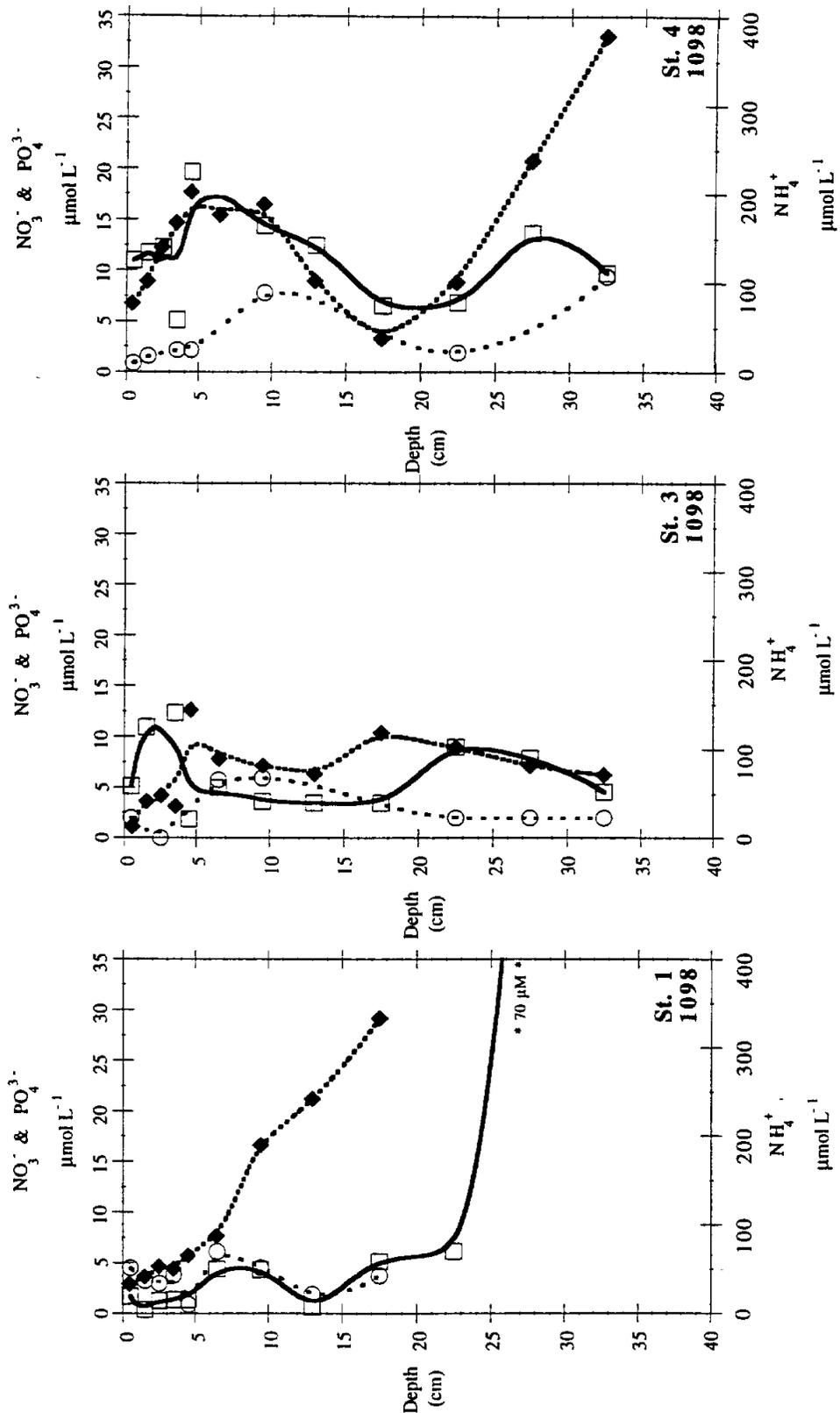
Figure 13: Pore water concentrations of ammonium (◆) [lower y axis] and nitrate+nitrite (O) and phosphate (□) [upper x axis] at Sta. 1, 3, 4, 5, Texas City and East Bay sites in November of 1998. Note that the scales of the two y-axes are different.

St. 5
1098

EB
1098

TC
1098
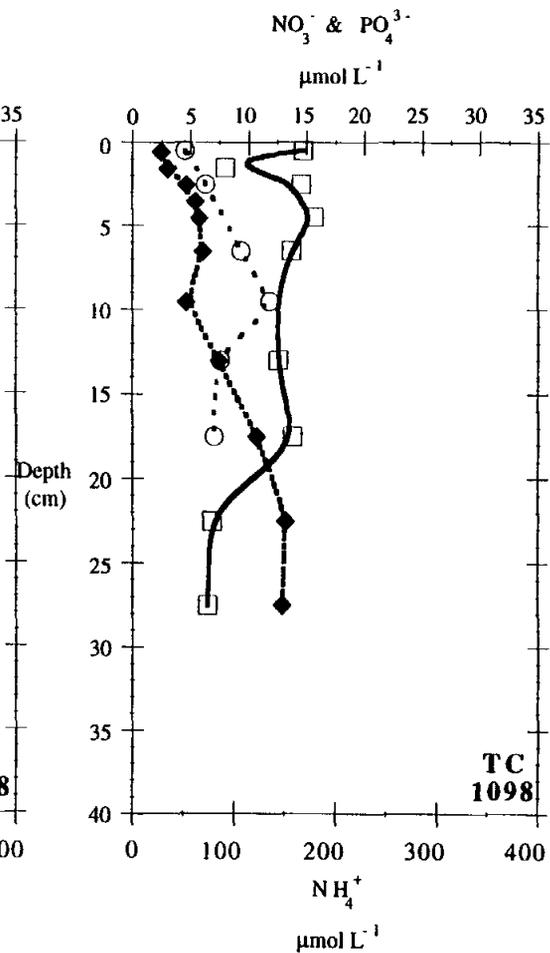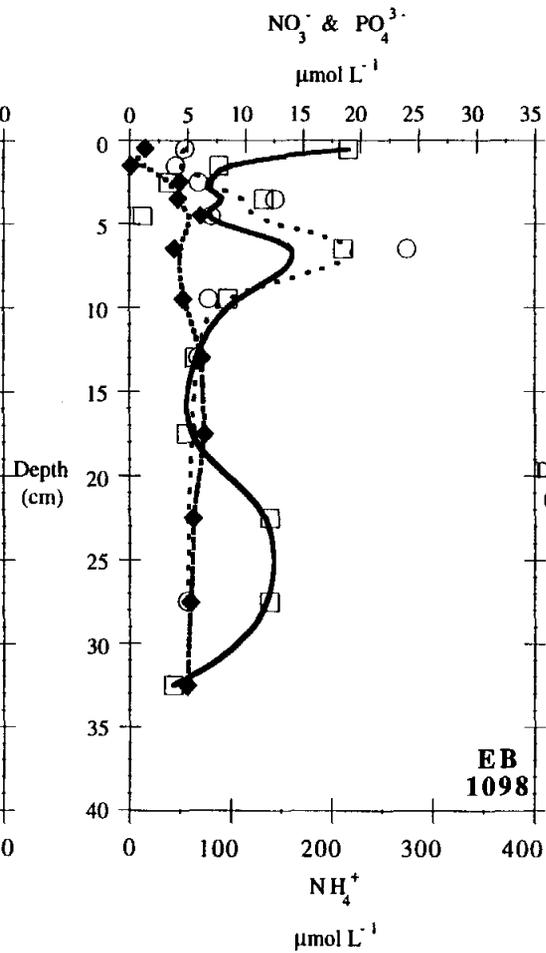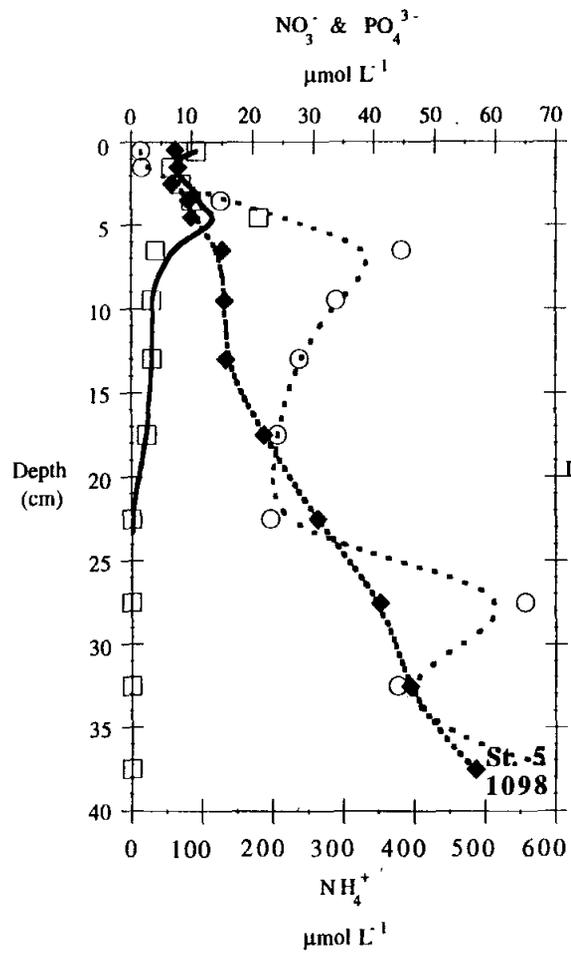
Benthic fluxes. A significant fraction of terrestrial nitrogen input to estuaries is lost via denitrification (Seitzinger 1988; Nixon et al. 1996; Nowicki et al. 1997). When denitrification is a major loss term, the process will either mitigate the impact of increased nitrogen loading or result in nitrogen 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 anthrophogenic perturbations (Brock et al. 1996).

Benthic primary production transforms regenerated inorganic nitrogen (NH_4^+ and 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 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 907×10^6 m^3 month^{-1}. The freshet (high amount of freshwater input) usually occurs during winter and spring. The average input at this time is 1370×10^6 m^3 month^{-1} (An 1999). During summer and fall, there is a dramatic decrease of freshwater input (140-580 $\times 10^6$ m^3 month^{-1}). In the first year of our study, 1996, the freshwater input was averaged 179×10^6 m^3 month^{-1}. Hydraulic residence time (t), estimated from the freshness (f), the volume of the bay (V) and the freshwater inflow (Q; t = f*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 (N loading (10^6 mole N) = 2.7689 × freshwater discharge ($10^6\,m^3$ 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 168×10^6 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 NH_4 uptake by sediments contradicted the calculated flux based on pore water profiles (An 1999). Benthic primary producers probably consume 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 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 mg chl. *a* m^{-2} (An 1999). While these chlorophyll concentrations are lower than those typical of benthic microalgal mats (10^3 -10^6 mg chl. *a* 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 $19 - 65$ mmole O_2 m^{-2} 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 mmole O_2 m^{-2} 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 mmole O_2 m^{-2} 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 (50-500 mmole O_2 m^{-2} 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 mmole N_2 m^{-2} d^{-1} (Table 3). The highest rate, 4.58 mmole m^{-2} d^{-1}, was measured in Nov. 1997 at Station 1 (Table 4). During summer, rates were high as was variability between sites (1.93 mmole m^{-2} d^{-1} at Texas City to 4.32 mmole m^{-2} 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 mmole m^{-2} day^{-1} in Jan. 1997 and 1998, respectively) and low in Texas City (0.58 and 0.78 mmole m^{-2} 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⁻²d⁻ in Galveston Bay. Positive values represent the fluxes out of sediment. Grain size (% sand) and salinity (ppt), temperature (° C), NO_3 and NH_4 concentration of bottom water are also presented. *ND* : no data.

Month	Station	sand (%)	salinity (ppt)	Temp. (°C)	[NO₃] (μM)	[NH₄] (μM)	N₂	NO₃ +NO₂	NH₄	O₂	DIC
Jun-96	ST4	14	15	27	*ND*	*ND*	1.67	*ND*	*ND*	*ND*	*ND*
Aug-96	ST2	98	1.5	30	2.7	14.0	2.04	-0.25	2.97	-2.04	*ND*
	ST3	17	12		2.1	14.0	1.31	-0.17	-1.83	-18.97	*ND*
	Texas City	87	17		0.8	0.0	1.04	0.04	0.28	-10.39	*ND*
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	*ND*	2.60	-0.19	*ND*	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	*ND*	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	*ND*	0.00	0.49	7.40	12.09
	ST4	*ND*	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	*ND*	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	*ND*	0		39.1	*ND*	1.47	-0.64	*ND*	-9.30	*ND*
	Texas City	83	13		20.5	*ND*	0.78	-1.95	*ND*	-1.03	11.68
Apr-98	ST1	*ND*	0	18	44.0	0.0	1.40	-0.83	0.85	-1.39	*ND*
	ST3	*ND*	0		44.6	0.0	2.62	-2.10	1.30	16.83	*ND*
	ST4	*ND*	0		41.0	0.0	2.79	*ND*	*ND*	0.97	*ND*
	East Bay	*ND*	2		21.6	7.8	1.06	0.06	-0.36	1.61	*ND*
	Texas City	*ND*	2.5		2.6	4.8	0.44	-0.06	1.55	1.55	*ND*
	Ship Chan.	*ND*	5		*ND*	3.2	1.43	0.07	2.58	-3.95	*ND*
Aug-98	East Bay	*ND*	20.4	31	0.4	13.0	0.99	0.00	1.99	-10.16	*ND*
	Texas City	*ND*	31.3		0.8	3.0	1.05	0.01	1.69	-6.68	*ND*
	Ship Chan.	*ND*	31		0.6	1.2	1.94	0.01	1.90	-6.99	*ND*
Oct-98	ST1	*ND*	0	20	10.7	4.1	2.23	-0.23	-0.08	-2.26	*ND*
	ST3	*ND*	0		10.2	7.9	0.11	-0.16	0.89	-6.20	*ND*
	ST4	*ND*	5.8		10.3	16.1	3.42	-0.18	1.42	-4.71	*ND*
	ST5	*ND*	6.4		20.0	14.2	1.37	0.08	0.41	-3.00	*ND*
	East Bay	*ND*	11.4		15.9	1.7	0.84	-0.66	0.45	-4.27	*ND*
	Texas City	*ND*	19.5		11.9	1.8	0.47	0.25	0.28	-2.65	*ND*

Table 4. Percent of denitrification supported by water column NO_3+NO_2 influx, nitrification, 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	N_2 Production supported by NO_3+NO_2 influx[a] (%)	Nitrification[b] (mmole m^{-2} d^{-1})	O_2 needed for Nitrification[c] (mmole m^{-2} d^{-1})	% of SOD	N efflux[d] (mmole m^{-2} d^{-1})	% benthic N efflux that is N_2[e]	R.Q.[f]
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
Average		25.5	2.6	5.1	109	2.5	71.7	3.7
Std dev		43.2	2.4	4.9	169	1.6	26.3	2.9

a: $(NO_3+NO_2$ flux$)/(N_2$ flux X 2)*100 only if there is NO_3+NO_2 flux into the sediment
b: Sum of NO_3+NO_2 flux and amount of NO_3+NO_2 needed to supply the measured rates of denitrification.
c: Stoichiometric ratio of 2 mole of O_2 needed to produce 1 mole of NO_3+NO_2
d: Sum of the positive fluxes of all N species (NO_3+NO_2, NH_4, N_2)
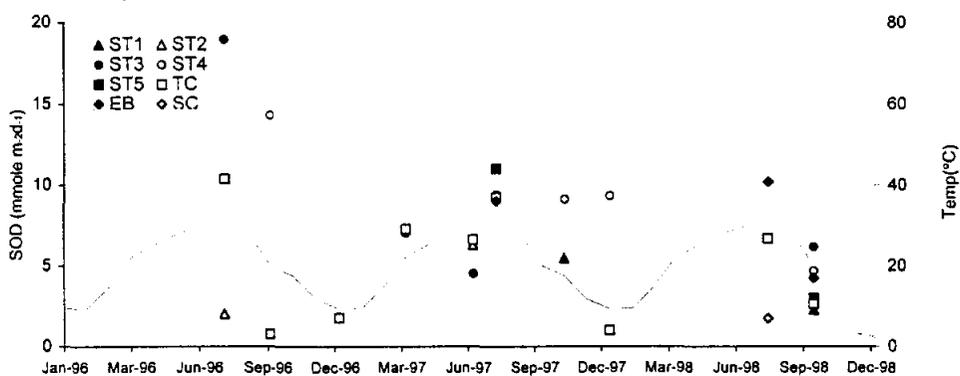e: N_2/N efflux *100
f: Respiratory Quotient = DIC/SOD
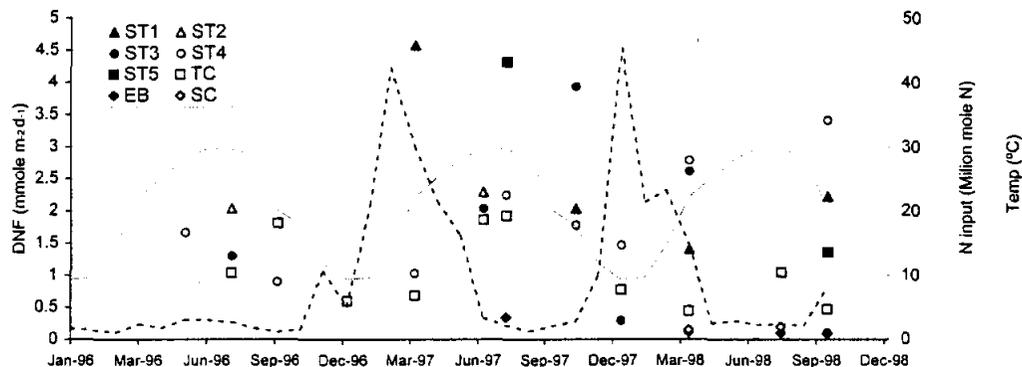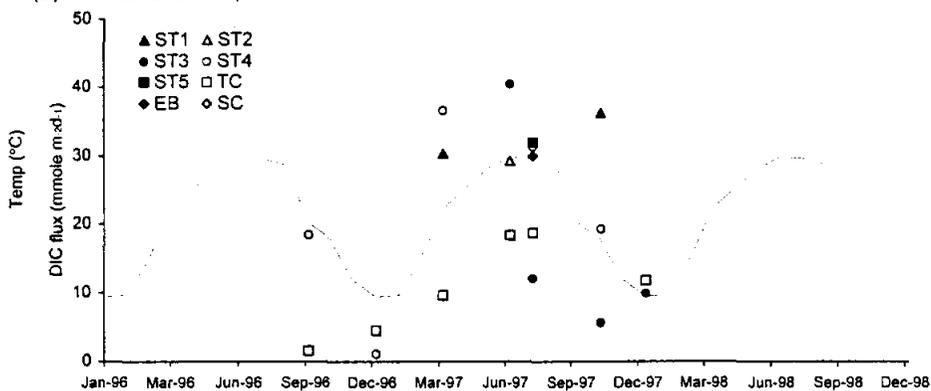
Figure 14. A. Temporal variation of denitrification rate (data points), N loading (dotted line), and temperature (solid line); B. DIC flux (data points) and temperature (solid line); and C. sediment oxygen demand (SOD; data points) and temperature (°C). Legends provide site identification.

stations were very high (4.32 and 3.21 mmole $m^{-2}day^{-1}$ at St. 5 and East Bay, respectively). The high DIC flux and SOD (sediment oxygen demand) and NH_4 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_2 depletion in bottom waters was observed during Aug. 1998.

The percent of denitrification supported by water column $NO_3 + NO_2$ versus that supported by in situ nitrification varies with time and space (Table 4). Water column NO_3 supported denitrification completely on several occasions. For example, during April 1997 and January 1998, when the water column NO_3 concentration was high (20.5 − 45 µM) due to increased freshwater discharge, NO_3 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_3 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_3 uptake by the sediments in 1998 relative to 1997.

Benthic NO_3 fluxes were almost always directed into the sediments, however the fluxes were usually small compared to the total N_2 flux. The NO_3 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_3 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 NO_3 is still abundant. Spring plankton blooms rapidly exhaust riverine 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 NH_4 and O_2 (Henriksen and Kemp 1988). Since 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 NH_4 regeneration is highest (MacFarland and Herbert 1984; Jenkins and Kemp 1984). Kemp et al. (1990) observed summer time maximum concentrations of NH_4 and N_2 flux when O_2 was not limiting. Though a seasonal trend in the 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 N_2 and NO_3 flux data, assuming there was no NO_3 or NO_2 reduction to 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 O_2 consumption, to estimate 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 N_2 (Table 4, calculations explained on the table).

The average nitrification rate in Galveston Bay sediments is 2.6 mmol m^{-2} d^{-1}; this value is higher than the Bay average denitrification rate (1.8 mmol m^{-2} d^{-1}). The average N flux from Galveston Bay sediments is 2.5 1.8 mmol m^{-2} d^{-1} and, of that, 72% is N_2 gas (Table 4). The nitrification rate ranged between 0 and 9.6
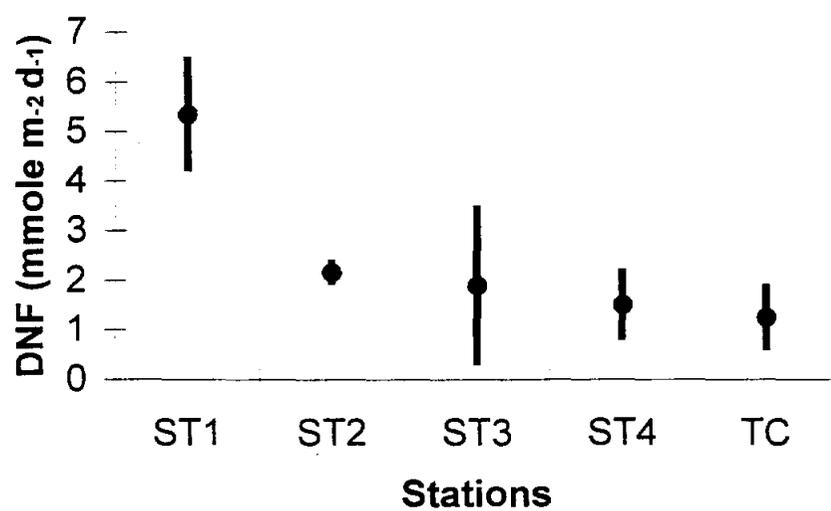
Figure *15.* Annual average denitrification rate (circle) and standard deviation (bar) in Galveston Bay. See Figure 1 for the locations of stations. TC=Texas City. Stations are arranged from low (ST1) to high (TC) salinity.

mmole $m^{-2} d^{-1}$ and exhibited distinct seasonal variation. The rate was high during summer (avg. = 4.7 mmole $m^{-2} d^{-1}$) and low during winter (avg. = 0.93 mmole m^{-2} d^{-1}). Interestingly, nitrification was low during Apr-97 (avg. = 1.2 mmole $m^{-2} d^{-1}$) when the water column NO_3^- 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_2 demand resulting from nitrification accounts for 109% of the measured SOD (Table 3, Table 4). In coastal environments, O_2 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_2 consumption by nitrifiers is exceptionally high compared with other estuaries and previous estimates, a value exceeding 100% of SOD requires an additional O_2 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_2 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 $m^{-2} day^{-1}$) 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 NO_3 and 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 O_2 and DIC flux
(respiratory quotient =11.7) and large influx of NO_3 that exceeded the 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 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 NO_3
concentration in Jan. 98.

Despite the lack of net O_2 production, the discrepancy between 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_2 concentration on denitrification is complicated by the fact that though increased NO_3 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 rexoidation 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_2 is the primary oxidant, even if part of the O_2 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 $m^{-2} d^{-1}$) and the highest rate (40.5 mmole $m^{-2} d^{-1}$) 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_2 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 mmole $m^{-2} d^{-1}$ for DIC and

6.9 mmole $m^{-2} d^{-1}$ for the SOD. While the SOD is 50% higher than previous

measurements in Galveston Bay (average SOD = 4.6 mmole $m^{-2} d^{-1}$; Zimmerman

and Benner 1994), DIC production is about 4 times larger than the previous

measurement (4.3 mmole $m^{-2} d^{-1}$). 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 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_2 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_2 flux will be the net result of organic matter decay <u>and</u> 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_2 and CO_2 flux besides remineralization, e.g. photosynthesis, could explain this negative relationship.

Benthic photosynthesis consumes CO_2 and produces O_2. When the R.Q. is exactly 1, and the photosynthetic quotient (P.Q. = O_2 production / CO_2 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 (ϕ) of photosynthesis, the net fluxes of O_2 and CO_2 are:

CO_2 flux $= rCO_2 - \phi \times pCO_2$

and

O_2 flux $= rO_2 - \phi \times pO_2$

Since $rCO2 = rO_2$, $pCO_2 = pO_2$, the result is R.Q.=1.

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

CO_2 flux $= rCO_2 - \phi \times pCO_2$

and

O_2 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 NH_4^+ is nitrogen source) and 2.0-2.5 (when 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 mmole $m^{-2}d^{-1}$). The moles of ammonia needed to assimilate one mole of CO_2 (α) 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 α.. Molar ratios between O_2 and NH_4 (β) and between CO_2 and N_2 production (γ) 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 NH_4 since it was well known that phytoplankton prefer NH_4 to NO_3 and it is unlikely that 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:

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

$$O_2 \text{ flux} = - R/R.Q. + P \times P.Q. - \beta \times N \quad \text{----------------------} \quad (2)$$

$$NH_4 \text{ flux} = R/C2N - P/C2N - N \quad \text{--------------------------------} \quad (3)$$

$$NO_3 \text{ flux} = Nit - 2 \times D \quad \text{--} \quad (4)$$

The four model equations can be solved simultaneously using the observed DIC, O_2, NH_4 and NO_3 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_3 flux) or denitrification rates (from Table 3). However, the average modeled rate of nitrification (2.56 and 2.67 mmol m^{-2} d^{-1} for RQs of 1 and 2 respectively) was similar to the average nitrification rate obtained from field data (2.6 mmol m^{-2} d^{-1}). 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^{-2} d^{-1}. 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 (mmole $m^{-2}d^{-1}$) 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	*ND*	*ND*	*ND*	*ND*	*ND*
	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	**negative solutions**					**negative solutions**				
	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	**negative solutions**				
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	*ND*	*ND*	*ND*	*ND*	*ND*	*ID* *ND*	*ND*	*ND*	*ND*	*ND*
	Texas City	*ND*	*ND*	*ND*	*ND*	*ND*	*ID* *ND*	*ND*	*ND*	*ND*	*ND*
Average		**40.88**	**22.70**	**2.57**	**1.24**	**0.53**	**27.37**	**8.45**	**2.67**	**1.29**	**0.30**

explain the observed DIC and O_2 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_2 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_3) 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_4 produced during organic matter degradation. Whether benthic primary producers compete with nitrifiers for NH_4 (thereby inhibiting nitrification) or provide O_2 for them (thereby enhancing nitrification) (Henriksen and Kemp 1988) appears to vary seasonally in Galveston Bay. Increased O_2 availability due to benthic primary production has been shown to enhance nitrification in other systems (Risgaard-Petersen et al. 1994) as well as
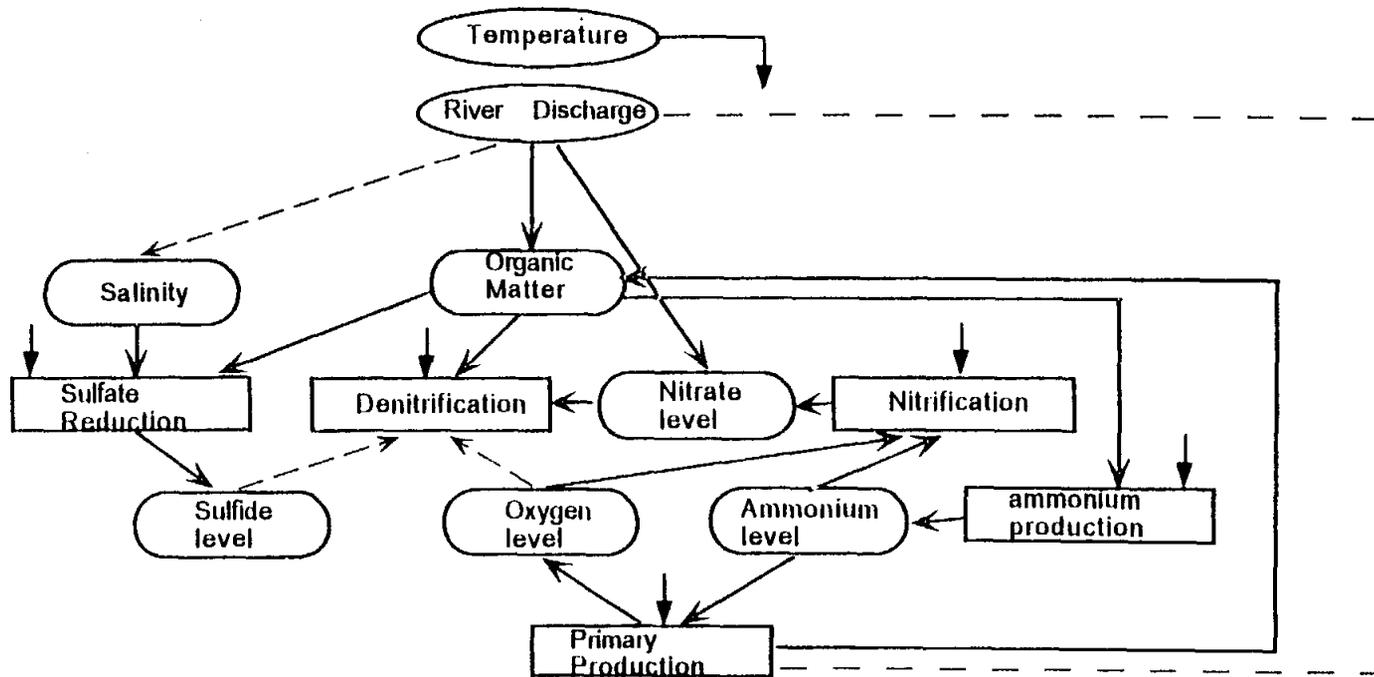
Figure 16. Conceptual relationships between various processes emphasizing denitrification. Solid arrows represent positive effect, while broken arrows represent negative effect.

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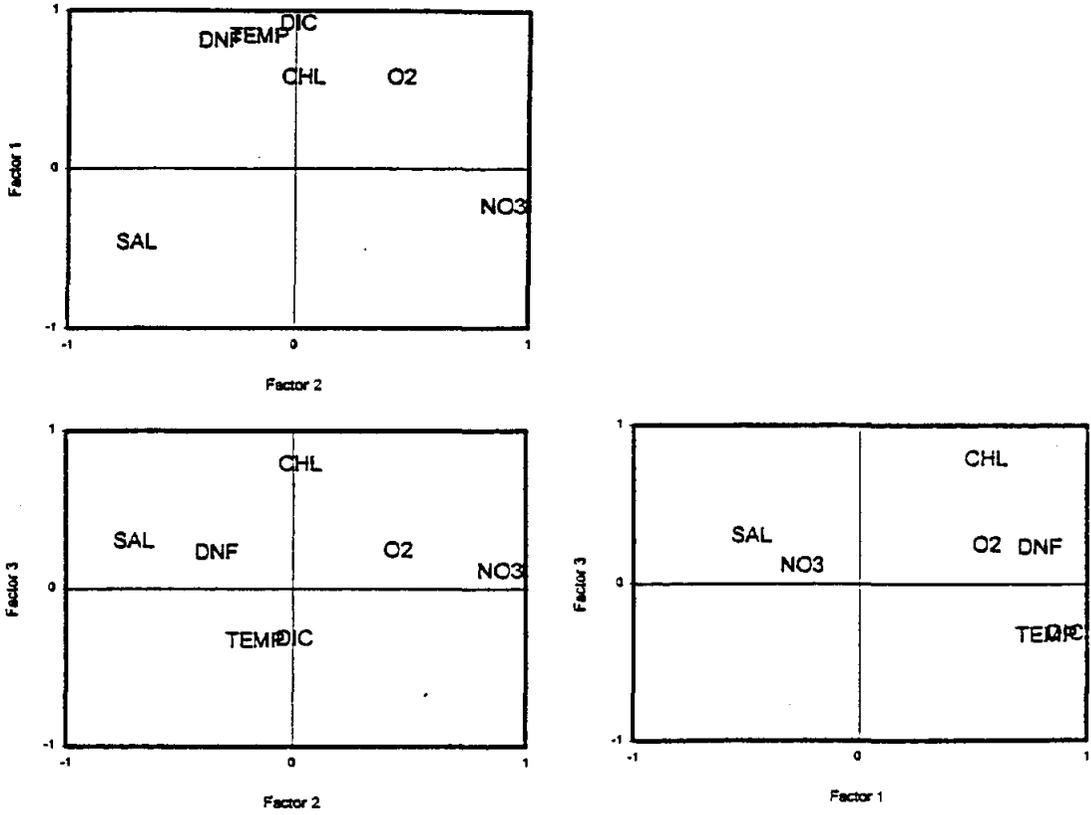
Figure 17: Results of the PCA analysis. DNF: denitrification; O2: sediment oxygen demand; DIC: DIC flux; CHL: sediment chlorophyll _a_; SAND: % sand; LOAD: freshwater input; TEMP: temperature; and, SAL: salinity.

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 8.3×10^7 mol N month^{-1}. 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,
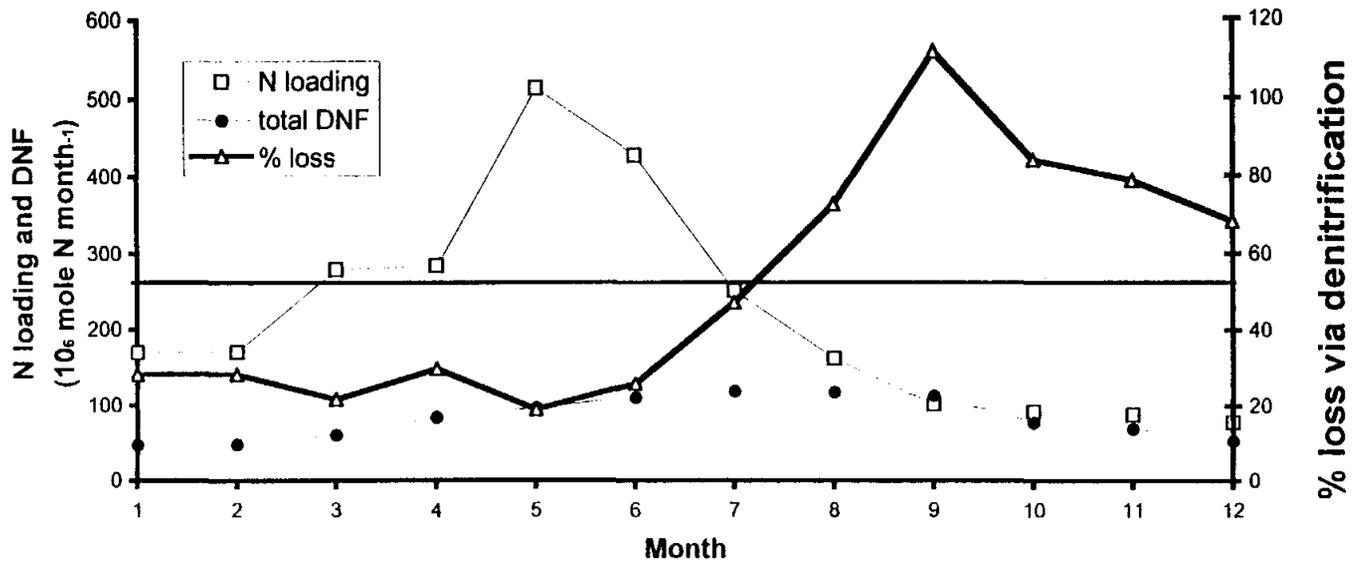
Figure 18. Whole system denitrification, nitrogen loading and % loss via denitrification in Galveston Bay. The rate was calculated using the denitrification rate in the relationship: DNF = a x 10(b x temp). Horizontal line represents the average removal (%).

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 (3680×10^6 g N year^{-1}) 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^{-1}.

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

to 14000×10^6 g N year^{-1} and remainder decreases from -1740 to -12063×10^6 g N year^{-1} 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 (Shipley & 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 30000×10^6 g N year^{-1} (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 mg Chl a 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 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^{-2} d^{-1}, respectively. Both DIC and N$_2$ 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$_3^-$ 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$_2$ by respiration (and nitrification). Benthic photosynthesis provided the O$_2$ required to support aerobic respiration and nitrification in Galveston sediment. Most of the NO$_3^-$ 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$_3$ concentration was high, than during summer and fall, when the water column NO$_3$ 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$_2$ 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 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 $170 * 10^6$ 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

V. References

An, S. 1999. Nitrogen cycling and denitrification in Galveston Bay. Ph. D. Dissertation, Texas A & M University, College Station, TX, 235 pp.

An, S. and S. B. Joye. 1997. An improved gas chromatographic method for measuring nitrogen, oxygen, argon and methane in gas or liquid samples. Marine Chemistry 59 (1,2): 63-70.

Andersen, T. K., M. H. Hensen and J. Sørensen. 1984. Diurnal variation in nitrogen cycling in coastal marine sediments. I. Denitrification. Mar. Biol. 83:171-176.

Armstrong, N. E. 1982. Responses of Texas estuaries to freshwater inflows. Pg. 103-120. In: Kennedy, V.S. (Ed.) Estuarine Comparisions. Academic Press, N. Y.

Armstrong, N. E. 1987. The ecology of open-bay bottoms of Texas: A community profile. U.S. Fish and Wildlife Service, Biological Report, 85(7.12).

Binnreup, S. J. and J. Sørensen. 1992. Nitrate and nitrite microgradients in barley rhizosphere as detected by a highly sensitive denitrification bioassay. Appl. Environ. Microbiol. 58:2375-2380.

Blackburn, T. H. and J. Sørensen. 1988. Nitrogen cycling in coastal marine environments, SCOPE 33, John Wiley & Sons, New York.

Boudreau, B. P. 1996. A method of line code for carbon and nutrient diagenesis in aquatic sediments. Computer Geosci. 22: 479-496.

Boudreau, B. P. 1997. Diagenetic models and their implementation. Springer Verlag Publishers.

Boudreau, B. P, and D. A. Canfield. 1988. A provisional diagenetic model for pH in anoxic sediment porewaters: application to the FOAM site. J. Mar. Res. 46: 429-455.

Brock, D. A., R. S. Solis and W. L. Longley. 1996. Guidelines for water resources permitting: nutrient requirements for maintenance of Galveston Bay productivity. EPA Final Report X-996024-01-2, 128 pp.

Caffrey, J. M. 1995. Spatial and seasonal patterns in sediment nitrogen remineralization and ammonium concentrations in San Francisco Bay, California. Estuaries 18(1B):319-233.

Caffrey, J. M. and W. M. Kemp. 1990. Nitrogen cycling in sediments with estuarine populations of Potamogeton perfoliatus and Zostera marina. Mar. Ecol. Prog. Ser. 66:147-160.

Capone, D. G. and R. P. Kiene. 1988. Comparison of microbila dynamics in marine and freshwater sediments: contrast in anaerobic carbon metabolism. Limnol. Oceanogr. 33: 725-749.

Christensen, J.P., J. W. Murray, A. H. Devol and L. A. Codispoti. 1987. Denitrification in continental shelf sediments has major impact on the oceanic nitrogen budget. Glob. Biogeochem. Cyc., 1(2): 97-116.

Cole, J. A., Fergusen, S. J. 1988. The Nitrogen and Sulfur Cycles, Society of General Microbiology, Cambridge Univ. Press, Cambridge.

Dollar, S. J., S. V. Smith, S. M. Vink, S. Obrebski and J. T. Hollibaugh. 1991. Annual cycle of benthic nutrient fluxes in Tomales Bay, California, and contribution to the benthos to total ecosystem metabolism. Mar. Ecol. Prog. Ser. 79: 115-125.

Falkowski, P. G. and J. A. Raven. 1997. Aquatic Photosynthesis. Blackwell Science.

Fenchel, T and B. J. Straarup. 1971. Vertical distribution of photosynthetic pigments and the penetration of light in marine sediments. OIKOS 22: 172-182.

Garcia, V. M. and D. A. Purdie. 1994. Primary production studies during a Gyrodinium cf. Aureolum (Dinophyceae) bloom in the western English Channel. Mar. Biology. 199(2): 297-305.

Grundmanis, V. and J. W. Murray. 1977. Nitrification and denitrification in marine sediments from Puget Sound. Limnol. Oceanogr. 22:804-811.

Hargrave, B. T. and G. A. Phillips. 1981. Annual in situ carbon dioxide and oxygen flux across a subtidal marine sediment. Estuar. Coast. and Shelf Sci. 12: 725-737.

Henriksen, K. and W. M. Kemp. 1988. Nitrification in estuarine and coastal marine sediments, pp. 207-249. In Blackburn, T. H. and J. Sørensen. (Eds.), Nitrogen cycling in coastal marine environments. SCOPE 33, John Wiley & Sons, New York.

Howarth, R. W., R. Marino, and J. Lane. 1988. Nitrogen fixation in freshwater, estuarine and marine ecosystems. I. Rates and Importance. Limnol. Oceanogr. 33: 669-687.

Howes, B. L., J. W. H. Dacey and G. M. King. 1984. Carbon flow through oxygen and sulfate reduction pathways in salt marsh sediments. Limnol. Oceanogr. 29(5): 1037-1051.

Jenkins, M. C. and W. M. Kemp. 1984. The coupling of nitrification and denitrification in two estuarine sediments. Limnol. Oceanogr. 29: 609-619.

Jørgensen, B. B. 1977. The sulfur cycle of coastal marine sediments (Limfjorden, Denmark). Limnol. Oceanogr. 22(3): 814-832.

Jørgensen, K. and J. Sørensen. 1985. Seasonal cycles of O_2, NO_3 and SO_4 reduction in estuarine sediments. The significance of a nitrate reduction maximum in spring. Mar. Ecol. Prog. Ser. 24: 65-74.

Joye, S. B. and H. W. Paerl. 1993. Contemporaneous nitrogen fixation and denitrification in marine microbial mats: Rapid response to runoff events. Mar. Ecol. Prog. Ser. 94: 267-274.

Joye, S. B. and J. T. Hollibaugh. 1995. Sulfide inhibition of nitrification influences nitrogen regeneration in sediments. Science 270: 623-625.

Joye, S. B. and S. An. 1997. Denitrification in Galveston Bay: 1996 Annual Report. Texas Water Development Board. 46 pp.

Joye, S. B. and S. An. 1998. Denitrification in Galveston Bay. 1997 Annual Report. Texas Water Development Board. 50 pp.

Joye, S. B., M. L. Mazzotta and J. T. Hollibaugh. 1996. Community metabolism in intertidal microbial mats: the importance of iron and manganese reduction. Estuar. Coast. Shelf Sci 43: 747-766.

Joye, S.B., S. V. Smith, J. T. Hollibaugh and H. W. Paerl. 1996. Estimating denitrification rate in estuary sediments: A comparison of stochiometric and acetylene based methods. Biogeochem. 33: 197-215.

Joye, S. B., J. T. Hollibaugh, H. W. Paerl and S. V. Smith. 1999. Nitrification and denitrification in the sediments of Tomales Bay, California (USA). Estuaries (in revision).

Kemp, W. M. and W. R. Boynton. 1981. External and internal factors regulating metabolic rates of an estuarine benthic community. Oecologia 51: 19-27.

Kemp, W. M., P. Sampou, J. Caffrey, M. Mayer, K. Henriksen and W. R. Boynton. 1990. Ammonium recycling versus denitrification in Chesapeake Bay sediments. Limnol. Oceanogr. 35: 1545-1563.

Knowles, R. 1982. Denitrification. Microbiol. Rev. 46(1):43-70.

Koike, I. and A. Hattori. 1979. Estimates of denitrification in sediments of the Bering Sea Shelf. Deep-Sea Res. 26: 409-415.

Koike, I. and J. Sørensen. 1988. Nitrate reduction and denitrification in marine sediments, p. 251-273. In Blackburn, T. H., Sørensen, J. (Eds.), Nitrogen cycling in coastal marine environments. SCOPE 33, John Wiley & Sons, New York.

Krause-Jensen, D. and K. Sand-Jensen. 1998. Light attenuation and photosynthesis of aquatic plant communities. Limnol. Oceanogr. 43(3): 396-407.

Kristensen, E. 1988. Benthic fauna and biogeochemical processes in marine sediments: Microbial activities and fluxes, p. 275-299. In Blackburn, T. H., Sørensen, J. (Eds.), Nitrogen cycling in coastal marine environments. SCOPE 33, John Wiley & Sons, New York.

Lin, S. and J. W. Morse. 1991. Sulfate reduction and sulfide mineral formation in Gulf of Mexico anoxic sediments. Amer. Jour. Sci. 291: 55-89.

MacFarland, G. T. and R. A. Herbert. 1984. Dissimilatory nitrate reduction and nitrification in estuarine sediments. J. Gen. Microbiol. 130: 2301-2308.

McClelland, J. W. and I. Valiela. 1997. Nitrogen stable isotope signature in estuarine food webs: A record of increasing urbanization in coastal watersheds. Limnol. Oceanogr. 42(5): 930-937.

McNicol, A. P., C. Lee and E. R. M. Druffel. 1988. Carbon cycling in coastal sediments: 1. A quantitative estimate of the remineralization of organic carbon in the sediments of Buzzards Bay, MA. Geochim. Cosmochim. Acta. 52: 1531-1543.

Morse, J. W. and R. A. Berner. 1994. What determines sedimentary C/S ratios? Geochim. Cosmochim. Acta. 35: 37-45.

Nishio, T., I. Koike and A. Hattori. 1982. Denitrification, nitrate reduction, and oxygen consumption in coastal and estuarine sediments. Appl. Environ. Microb. 43:648-653.

Nishio, T., I. Koike and A. Hattori. 1983. Estimates of nitrification and denitrification in coastal and estuarine sediments. Appl. Environ. Microb. 45:444-450.

Nowicki, B. L., 1994. The effect of temperature, oxygen, salinity, and nutrient enrichment on estuarine denitrification rates measured with a modified nitrogen gas flux technique. Estuar. Coast. Shelf. Sci., 38: 137-156.

Nixon, S. W., et al. 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochem. 35:141-180.

Nowicki, B. L., J. R. Kelly, E. Requintina and D. Van Keuren. 1997. Nitrogen losses through sediment denitrification in Boston Harbor and Massachussetts Bay. Estuaries 20:626-639.

Pind, A., N. Risgaard-Peterson and N. P. Revsbech. 1997. Denitrification and microphytobenthic nitrate consumption in a Danish lowland stream: diurnal and seasonal variation. Aquatic Microbiol. Ecol. 12: 275-284.

Pinckney, J. and R. G. Zingmark 1991. Effects of tidal stage and sun angles on intertidal benthic microalgal productivity. Mar. Ecol. Prog. Ser. 76: 81-89.

Pinckney, J. L. and R. G. Zingmark. 1993. Modeling the annual production of intertidal benthic microalgae in estuarine ecosystems. J. Phycol. 29: 396-407.

Revsbech, N. P., J. Sørensen and T. H. Blackburn. 1980. Distribution of oxygen in marine sediments measured with microelectrodes. Limnol. Oceanogr. 25: 403-411.

Revsbech, N. P., J. Nielsen and P. K. Hansen. 1988. Benthic primary production and oxygen profiles. Chapter 4. In: Blackburn, T. H. and J. Sørensen (Eds.) Nitrogen cycling in coastal marine environments. John Wiley & Sons.

Risgaard-Petersen, N., S. Rysgaard, L. P. Nielsen and N. P. Revsbech. 1994. Diurnal variation of denitrification and nitrification in sediments colonized by benthic microphytes. Limnol. Oceanogr. 39(3): 573-579.

Robertson, L. A and J. G. Kuenen. 1991. Physiology of nitrifying and denitrifying bacteria, p. 189-199. In Rogers, J. E., Whitman, W. B. (Eds.), Microbial production and consumption of greenhouse gases: methane, nitrous oxide, and halomethanes. American Society of Microbiology Press, Washington, D.C.

Rowe, G. T., C. H. Clifford, J. K. Smith and P. L. Hamilton. 1975. Benthic nutrient regeneration and its coupling to water column primary productivity in coastal waters. Nature. 255: 215-217.

Rowe, G. T., and others. 1988. Benthic carbon budgets for the continental shelf south of New England. Cont. Shelf Res. 8: 511-527.

Rowe, G. T., G. S. Boland, J. Morse, C. Cooper, M. E. Cruz-Kaegi and E. E. Briones. (submitted) Benthic metabolism in Galveston Bay.

Ryther, J. M. and W. M. Dunston. 1971. Nitrogen, phosphorus and eutrophication in the coastal marine environment. Science. 171: 1008-1013.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystem: Ecological and geochemical significance. Limnol. Oceanogr., 33:702-724.

Seitzinger, S. P. 1990. Denitrification in aquatic sediments, pp. 301-322. In: Revsbech, N. P. and J. Sørensen (Eds.) Denitrification in soil and sediment. FEMS Symposium No. 56. Plenum Press.

Seitzinger, S. P., S. W. Nixon, M. E. Q. Pilson and S. Burke. 1984. Denitrification and nitrous oxide production in a coastal marine ecosystem. Limnol. Oceanogr. 30(6): 73-83.

Shipley, F. S. and R. W. Kiesling. 1994. The state of the Bay: A characterization of the Galveston Bay ecosystem. The Galveston Bay National Estuary Program Publication GBNEP-44.

Smith, K. L. and J. M. Teal. 1979. Deep-sea benthic community respiration: an in situ study at 1850 meters. Science. 282-283.

Sneath, P. H. A. and R. R. Sokal. 1973. Numerical taxonomy. W. H. Freeman and Company.o

Sørensen, J., B. B. Jørgensen and N. P. Revsbech. 1979. A comparison of oxygen, nitrate and sulfate respiration in coastal marine sediments. Micro. Ecol. 5: 105-115.

Tiedje, J. M., S. Simkins and P. M. Groffman. 1989. Perspectives on measurement of denitrification in the field including recommended protocols for acetylene --based methods. Plant Soil, 115: 261-284.

Tomaszek, J. A., W. S. Gardener and T. H. Johensen. 1997. Denitrificatoin in sediments of Lake Erie coastal wetland (Old Woman Creek, Huron, Ohio, USA). J. Great Lakes Res. 23: 403-415.

Vanberborght, J. P., Billen, G. 1975. Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification. Limnol. Oceanogr. 20:953-961.

Warnken, K. W. 1998. Sediment water exchange of trace metals and nutrients in Galveston Bay, Texas. M. S. Thesis. Texas A&M University, College Station, TX.

Wollast, R. 1983. Interactions in estuaries and coastal waters, p. 385-407. In: Bolin, B. and R. B. Cook (Eds.) The major biogeochemical cycles and their interaction. SCOPE

Zimmerman, A. R., Benner, R. 1994. Denitrification, nutrient regeneration and carbon mineralization in the sediments of Galveston Bay, Texas, USA. Mar. Ecol. Prog. Ser. 114: 275-288.

Zehnder, A. J. B. and W. Stumm. 1988. Geochemistry and biogeochemistry of anaerobic habitats, p. 1-38. In: Zehnder, A. J. B. (Ed.) Biology of anaerobic microorganisms. John Wiley & Sons.

Zumft, W. G., Viebrock, A., Körner, H. 1988. Biochemical and physiological aspects of denitrification, p. 245-279. In Cole, J. A., Ferguson, S. J. (Eds.) The Nitrogen and Sulfur Cycles, Society of General Microbiol., Cambridge University Press, Cambridge, England.