James L. Pinckney

System-scale nutrient fluctuations in Galveston Bay, Texas (USA)

Abstract

The purpose of this review is to identify and characterize the major estuarine nutrients, illustrate the annual to biweekly fluctuations of water column nutrients, and provide insights into the major factors that regulate the spatio-temporal distributions of nutrients in a typical subtropical estuary in the Gulf of Mexico, Galveston Bay, Texas. Decadal and annual estimates of total N loading highlight the importance of interannual variation and long-term trends, which are useful for developing nutrient input management strategies and assessing the effectiveness of mitigation programs. However, long-term averaging of large spatial areas dampens the frequency and magnitude of seasonal events and system perturbations. Shorter timescale measurements were undertaken to determine event-based nutrient fluctuations in Galveston Bay. Water samples were collected and hydrographic profiles were recorded at 9 stations at biweekly intervals from 1999 to 2002 along a fixed transect. Sample analyses included nutrient concentrations, phytoplankton biomass, and phytoplankton community composition. Data were analyzed using spatio-temporal contour plots. The results showed that nutrient concentrations in this estuary reflected a balance between river discharge, benthic regeneration, and water temperature (season). Major perturbations, such as the passage of tropical storm Allison, upset this balance and profoundly changed the biogeochemistry of the estuary. After this 'flushing' event, the system seemed to slowly return to a 'normal' pattern of nutrient distributions. Documenting nutrient fluctuations in estuaries is relatively straightforward provided the funding, resources, and time are available. Understanding the relative importance of the different processes driving these fluctuations on a system scale is a much more formidable task. Mechanistic studies of benthic and planktonic biogeochemical processes, coupled in space and time, are a necessary prerequisite for developing reliable models to simulate, and possibly predict, estuarine nutrient fluctuations.

Introduction

Estuaries are semi-enclosed coastal bodies of water which have a free connection with the sea and within which seawater is measurably diluted by freshwater. The freshwater sources for most estuaries are streams, rivers, and possibly groundwater.

In the continental US, estuaries comprise more than 80% of the coastline along the Atlantic Ocean and Gulf of Mexico and more than 10% of the Pacific coast (Bricker *et al.* 1999). Most estuaries are very efficient at retaining dissolved and particulate matter (Hobbie 2000). In this respect, estuaries are often thought of as filters or traps that are located between the land and the sea. Because these systems are so efficient at retaining dissolved chemicals and particulates, they are very susceptible to nutrients and pollutants that are washed into the estuary (*NRC* 2000). These chemicals typically have long residence times in estuaries and tend to accumulate over time. High rates of nutrient inputs from land runoff stimulate primary production and thereby increase the rate of organic matter loading in the estuary. Excessive nutrient loading can lead to primary production that exceeds the assimilative capacity of the system and consequently leads to eutrophication (Nixon 1995). The purpose of this review is to identify and characterize the major estuarine nutrients, illustrate the annual to biweekly fluctuations of water column nutrients, and provide insights into the major factors that regulate the spatio-temporal distributions of nutrients in a typical subtropical estuary in the Gulf of Mexico, Galveston Bay, Texas

Overview of estuarine nutrients

As the conduit between the land and sea, estuaries are exposed to a variety of dissolved chemical species. Some of these compounds are used by resident biota and promote growth or provide energy for physiological processes such as photosynthesis and are considered nutrients. In estuaries, the most important nutrients for primary production are inorganic and organic nitrogen compounds, phosphate, silicate, and dissolved organic matter.

   Nitrogen (N) is a key constituent for life on Earth and this element occurs in many different chemical pools and states in the biosphere. All living organisms require N for the synthesis of amino acids and proteins for growth. Most of the N in marine waters is in the form of N_2 (dissolved dinitrogen gas) at a concentration of 1 mM (Pilson 1998). Concentrations of N_2 are relatively uniform in seawater but vary as function of the temperature-salinity dependent solubility of the gas (Pilson 1998). Nitrous oxide (N_2O) and nitric oxide (NO) are trace constituents in seawater, mostly due to microbial activity (Capone 2000). Nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+), collectively termed dissolved inorganic nitrogen (DIN), are the most abundant non-gaseous N species in estuarine waters (Sharp 1991; Alongi 1998). Nitrate is highly mobile and is usually the dominant form of N in runoff, riverine input, groundwater discharge, and atmospheric deposition. Nitrite is a minor component of the total DIN pool, but concentrations may be high at redox interfaces. Ammonium concentrations can vary widely in estuaries depending on season, location, and depth in the estuary. Furthermore, NH_4^+ concentrations are usually high in hypoxic/anoxic environments, near sewage/wastewater outfalls, in agricultural runoff, and in areas of high benthic biomass (e.g., oyster reefs, clam beds, etc.) (Dame *et al.* 1989). Ammonium is usually the dominant form of DIN in the porewater of

estuarine sediments. In estuaries, water column concentrations of DIN usually range from 0 to 100 μM (Hobbie 2000).

Dissolved organic nitrogen (DON) is a mixture of organic molecules, such as amino acids, nucleic acids, simple proteins, and urea, that contain N (Dortch 1990). However, the chemical identities of many of the compounds found in DON remain uncharacterized but most of the DON seems to be composed of refractory biopolymers (Ogawa *et al.* 2001). DON is a major N pool in estuarine systems but the biological utilization of DON as a source of N depends greatly on the amount of labile N in the total DON pool (Ward and Bronk 2001). DON sources in estuaries are the same as DIN sources but the ratios of DIN to DON vary depending on the source.

Like N, phosphorus (P) is an important chemical for life and is a major element in organic matter. In aerobic environments, phosphorus occurs almost exclusively as orthophosphate, which is any salt of H_3PO_4 (phosphoric acid). The dissociation products are $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} and the major ion in seawater is HPO_4^{2-} (Pilson 1998). Polyphosphates are formed when H_2O is removed by cellular processes, but these compounds are not commonly found in seawater except near sewage outfalls. Organophosphates are phosphate esters derived from living cells. Phosphate (as orthophosphate) is the most abundant form of P in estuarine and coastal waters (Alongi 1998; Pilson 1998). Phosphates readily adsorb onto particulates; under aerobic conditions, phosphate adsorbs onto oxyhydrides, calcium carbonates, and clay mineral particles, where phosphate is substituted for silicate in the lattice structure of clays (Pilson 1998). Phosphates also tend to form insoluble compounds with certain metals and readily precipitate with cations such as Ca^{2+}, Al^{3+}, and Fe^{3+} (francolite, hydroxyapatite) (Sharp 1991). In anaerobic environments, the combination of bacteria and H_2S results in the reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) and the release of dissolved phosphate. Ferric oxyhydroxides dissolve and solubilize phosphate. Thus interstitial porewaters usually have high phosphate concentrations except in carbonate sands (Milliman 1974; Alongi 1998). Some of the dissolved phosphate may reprecipitate at the oxic/anoxic interface and sediments may be a source of phosphate if the overlying waters are anoxic.

Silicon (Si), an important element for cell wall formation in diatoms, silicoflagellates, radiolarians, and some sponges, is a common element in clay particles and is usually present in high concentrations in estuaries. In marine waters, the common particulate form is silica (SiO_2) and the dissolved form is silicate [$Si(OH)_4$] (Pilson 1998). Biogenic silica, produced by organisms, exists as opaline, a non-crystalline form of hydrated silica. Under conditions of high N-loading or during large diatom blooms, silicate may become a limiting nutrient for diatoms (Fisher *et al.* 1992; Glibert *et al.* 1998).

Dissolved organic matter (DOM) is one of the largest organic carbon pools on earth and plays a central role in the biogeochemistry of a variety of elements in estuarine ecosystems (Farrington 1992). DOM is a mixture of a range of sizes of organic molecules which are usually characterized in terms of molecular weight fractions. In estuarine habitats, organic matter occurs in both particulate (POM; plant debris, detritus, phytoplankton) and dissolved forms (DOM; humics, mucopolysaccharides, peptides, lipids). The distinction between POM and DOM is arbitrary and

depends on the methods used to separate these two fractions (e.g., filtration, ultrafiltration, centrifugation, dialysis). In addition, the rates of supply of different forms of DOM are highly variable and are predicated by the land use characteristics of the watershed (rural, agricultural, urban, etc.), hydrology, and climatology (Guo *et al.* 1999). Sources of DOM can come from two major pathways. Allochthonous DOM originates outside the estuary and is transported into the estuary from watershed run-off, stream/wetland inflow, or anthropogenic point sources. Autochthonous DOM is generated within the system, mostly through photosynthesis by primary producers or by benthic regeneration of OM. In estuarine habitats, the dominant primary producers of autochthonous DOM are phytoplankton, benthic microalgae, epiphytes/periphyton, and submerged aquatic vegetation.

Riverine DOM is a mixture of inputs from watershed runoff, wastewater treatment facilities, and aquatic primary production (Burton and Liss 1976). Fluxes and concentrations of DOM (measured as DOC, dissolved organic carbon) into coastal waters can be substantial over annual time scales. For example, the average DOC concentration in large river systems in the Gulf of Mexico region ranges from 270 to 833 μM with loading rates of 0.1 to 209 x 10^{10} g C yr^{-1} (Guo *et al.* 1999). The pool of organic substances is dynamic. Some high molecular weight DOM can be rapidly recycled by bacteria (Amon and Benner 1994) while other compounds undergo photochemical degradation into more labile low molecular weight DOM (Kieber *et al.* 1989). In addition, the bioavailability of selected molecules in water appears to be altered from that observed in pure solution (Keil and Kirchman 1994), mainly because of the presence of DOM. Phytoplankton may secrete exopolymers to create conditions more favorable for growth, to regulate nutrient and trace metal availability, and for protection from toxic compounds (Moffett and Brand 1996; Ahner *et al.* 1997; Croot *et al.* 2000; Tang *et al.* 2001; Hung *et al.* 2001).

Different sources of DOM may have varying effects on phytoplankton communities. Many facultative autotrophs (mixotrophs), are able to supplement their cellular organic C requirements using DOM obtained from outside the cell (Bennett and Hobbie 1972; Droop 1974; Neilson and Lewin 1974; Hellebust and Lewin 1977; Gaines and Elbrächter 1987). DOM is also an important source of nutrients (e.g., glucose, urea, amino acids) for the growth and metabolism of heterotrophic bacteria in estuaries (Azam *et al.* 1983, 1993; Kirchman *et al.* 1991). The bacterial community may compete with phytoplankton for available inorganic nutrients, and, in the case of the presence of mixotrophic algae and/or heterotrophic flagellates, for the available DOM (Carlsson *et al.* 1998). These competitive interactions may be an important regulator of DOM transformations as well as a determinant of phytoplankton community structure and function (Sherr 1988).

Nutrient sources and sinks

New nutrients are nutrients that are supplied from outside a system while *regenerated* nutrients are derived from *in situ* chemical cycling within the estuary. The major sources of *new* nutrient inputs into estuaries are associated with freshwater flow into

the estuary. Dissolved nutrients in river discharge constitute the primary nutrient source for many estuaries that receive significant freshwater input. Nutrient inputs from identifiable sources such as sewage outfalls, industrial process water, and other 'pipes' are point sources. Non-point sources are those which cannot be defined as discrete points such as agricultural runoff or groundwater. In some regions, atmospheric deposition, as wet deposition (rain) or dry deposition (dust), may supply a significant quantity of nutrients, especially N, to the surface of the estuary (Paerl 1995; Prospero *et al*. 1996). Another potential source of *new* N in estuaries may be N fixation by resident prokaryotes (Paerl 1990). Groundwater may be a significant nutrient source, but quantifying the input rates from this source is difficult in estuarine habitats and is virtually unknown for many estuaries (Tobias *et al.* 2001). In estuaries that are surrounded by watersheds low in nutrients, nutrients may be imported from coastal waters through tidal exchange and gravitational flow. The major sources of *regenerated* nutrients are the benthos and recycling in the water column. The relative importance of these two sources depends on the water volume and benthic surface area of the estuary. In shallow estuaries, benthic processes tend to dominate while water column processes are more important in deeper estuaries (Hobbie 2000).

Although estuaries function as nutrient 'traps', there are four major sinks that are responsible for nutrient removal. In most estuaries (except negative estuaries), the net flow of water is out of the estuary. Thus some quantities of nutrients are exported to coastal waters and lost from the system. Tidal exchange volume, flushing time, and residence time are determinants of the importance of this export mechanism. Inorganic nitrogenous compounds such as nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) are removed from the system by microbial processes. Nitrification and denitrification result in the oxidation of NH_4^+ to NO_2^- to NO_3^- and the reduction of NO_3^- to gaseous forms such as nitrous oxide (N_2O) or dinitrogen gas (N_2). These two process are coupled in marine sediments, with nitrifying bacteria supplying the NO_2^- and NO_3^- used by denitrifying bacteria. The efficient coupling of nitrification-denitrification results in the conversion of bioavailable N forms to gaseous N_2 and is a primary mechanism for N losses in coastal ecosystems. However, nitrification is an aerobic process while denitrication is an anaerobic process. Under anoxic conditions, which are commonly found below 1 cm in sediments, organic N is regenerated by microbial processes (ammonification) to produce NH_4^+. In the absence of oxygen, or when nitrification rates are less than NH_4^+ supply rates, the primary form on N released from sediments is NH_4^+. Thus the nitrogen species and fluxes from sediments are a function of the rate balances of diffusion and microbial processes. In estuaries with high sedimentation rates, organic matter and nutrients may be buried deep in sediments and effectively removed from the system. However, severe wind events (e.g., hurricanes) or dredging activities may uncover these deeper sediments, allowing the reintroduction of nutrients into the estuary. Finally, fisheries harvests, which result in the removal of biota from the estuary, are another important but rarely quantified nutrient export mechanism.

The spatio-temporal fluctuations of water column nutrients are essentially unique to each estuary. For this review, Galveston Bay, Texas, an estuary typical for the Gulf of Mexico, was selected as a case study to illustrate estuarine nutrient fluctuations.

Galveston Bay

Galveston Bay is one of 7 major bays along the Texas coast and is the second largest estuary in the Gulf of Mexico (Figure 1). The drainage basin includes the metropolitan areas of Dallas/Fort Worth and Houston, Texas. The human population surrounding the bay exceeds 5 million people. Galveston Bay has a high socioeconomic value and is responsible for approximately one-third of the state's fishing income. Commercially important species include shrimp, blue crabs, and oysters. For example, the average annual oyster harvest for the bay is ca. 1,800 metric tons with a value of 8 million US dollars (Robinson *et al.* 2000).

Physical description

Galveston Bay (29.5°N, 94.8°W), a coastal plain estuary, has a surface area of 1,554 km^2 and is surrounded by 526 km^2 of marshland. A deep (12-14 m), but narrow (120-160 m) ship channel that serves the Port of Houston bisects the bay. With the exception of oyster reefs and dredge spoil banks, the bathymetry is generally flat and regular with water depths ranging from 2 to 3 m. Compared with other estuaries in the US, Galveston Bay has a small water volume relative to the benthic surface area (Figure 2). The shallow water column and broad, flat bottom create a situation in which the role of the benthos as a modulator of water column processes is likely enhanced in comparison with other estuaries.

The major freshwater inputs into the estuary are from the Trinity (83%) and San Jacinto (8%) Rivers (NOAA 1989). The tidal range in the bay averages 40 cm, is primarily diurnal, and fosters the long hydraulic residence time of the estuary (40-88 days) (Santschi 1995). Most of the tidal exchange (ca. 80%) in Galveston Bay occurs through Bolivar Roads at the mouth of estuary while a small, manmade cut through Bolivar Peninsula (Rollover Pass) provides minor circulation in East Bay (NOAA 1989). Tidal exchange in West Bay occurs through San Luis Pass. The low tide water volume of Galveston Bay is 2.50 x 10^9 m^3 and the intertidal volume is 2.10 x 10^8 m^3 (Lowery 1998). Thus, only 7.7% of the total water volume of the bay is exchanged by tidal processes. The absence of a strong tidal influence reinforces the potential importance of benthic/pelagic exchange in governing nutrient concentrations in Galveston Bay. The long-term average salinity for Galveston Bay is 15.5 psu and can range from 13.7 to 18.0 during low and high riverine discharge conditions, respectively (NOAA 1989; Lowery 1998). Furthermore, winds are more important than tides for circulation in Galveston Bay and the predominant wind direction is southeasterly. Bay circulation is generally anticyclonic during periods of high freshwater inflow and cyclonic during low inflow (NOAA 1989).

Sediments in the bay are composed primarily of mud (silt and clay) and sandy mud (NOAA 1989). The upper bay is underlain by shallow piercement salt domes that contain oil and gas deposits and, consequently, there are a number of active oil wells and platforms in Trinity Bay. An extensive analysis of trace metal concentrations in the water column and sediments of Galveston Bay found metal levels similar to more pristine bays elsewhere (Morse *et al.* 1993). Trace metal concentrations in
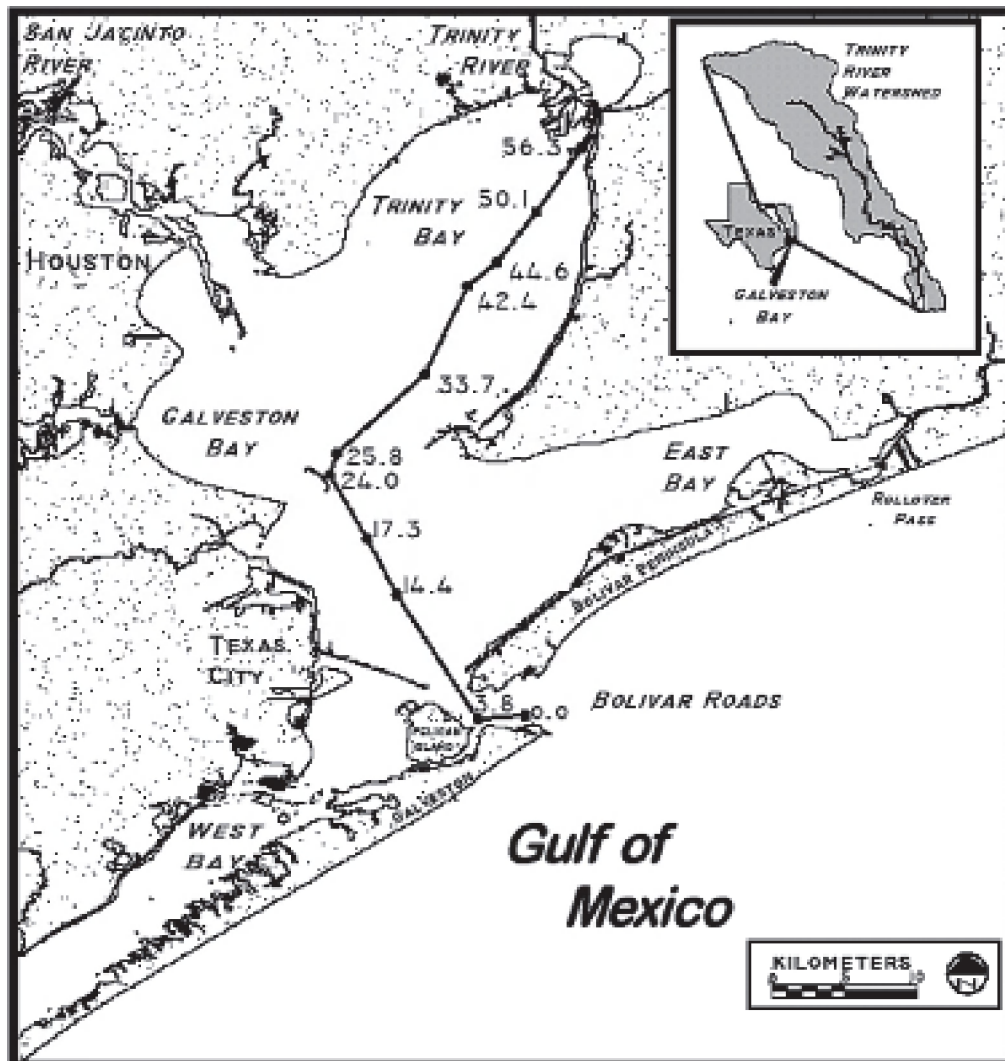
Figure 1. Location map for Galveston Bay, Texas (29.5°N, 94.8°W). The bay transect is denoted by the solid line and station locations are marked with numbers (0.0 to 56.3) corresponding to the distance (km) upstream from the mouth of the estuary.
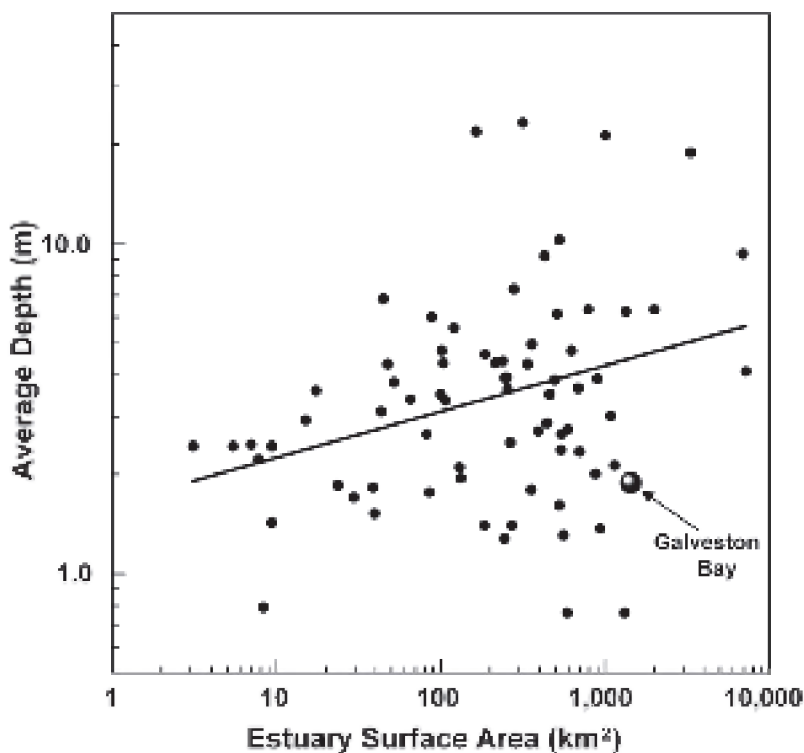
Figure 2. Plot of the average depth and surface area for 74 estuaries in the continental US. The solid line is a linear regression line for all points. Data from Bricker *et al.* 1999.

the water column were significantly correlated with concentrations of suspended particulate matter, suggesting that wind and tidal resuspension of sediments was the primary cause for elevated metal concentrations. In addition, many of the metals in the top 10 cm of sediment were coprecipitated with pyrite (Morse *et al.* 1993).

Long-term changes in nutrient concentrations

Improvements in municipal water treatment discharges into the San Jacinto River and the Houston Ship Channel have resulted in a shift from ammonium to nitrate as the primary source of N entering lower Galveston Bay (Crocker and Koska 1996). In the period from 1971 to 1991, there was an increasing trend in the loading of nitrate and nitrite from this source. However, overall water quality in the HSC improved markedly over the 20-year period (Crocker and Koska 1996). Criner and Johnican (2002), using data from the Texas Natural Resources and Conservation Commission (TNRCC), summarized the long term trends in water and sediment quality for Galveston Bay during the period from 1969 to 1999. Ammonium, nitrate-nitrite, and total

phosphorus concentrations declined over the period. They also reported a concomitant decline in the monthly average chlorophyll *a* concentration (phytoplankton biomass). Santschi (1995) examined the Texas Water Commission database (1980-1989) to determine the seasonality of water column nutrient concentrations in Galveston Bay. Phosphate concentrations exhibited a recurring seasonal maximum in September which was attributed to benthic regeneration of phosphorus at the end of summer. Nitrate concentrations were inversely correlated with salinity and suggested that the Trinity River was the major source of nitrate for the estuary (Santschi 1995).

Annual N loading

Stanley (2001) summarized nitrogen loading rates for Galveston Bay from 1977 to 1990. Estimates of total nitrogen ($NO_3^- + NO_2^- + TKN$) loading were determined using data from USGS river flow gage stations (gaged flows), ungaged watershed flows, wastewater (return flows), and wet deposition directly to the bay surface (rain) (Figure 3). Groundwater inputs were assumed to be insignificant and not included in the calculations. Over the 13-year period, N loading attributed to wastewater and rain was relatively constant. In contrast, gaged and ungaged flows were the primary sources of N loading. The high interannual variability in loading rates was attributed to rainfall in the drainage basin (Brock 2001). Using these data, Brock (2001) estimated that the mean annual load of total nitrogen to Galveston Bay was $38,350 \pm 11,488$ sd x 10^3 kg N y^{-1} with a total N load per unit surface area
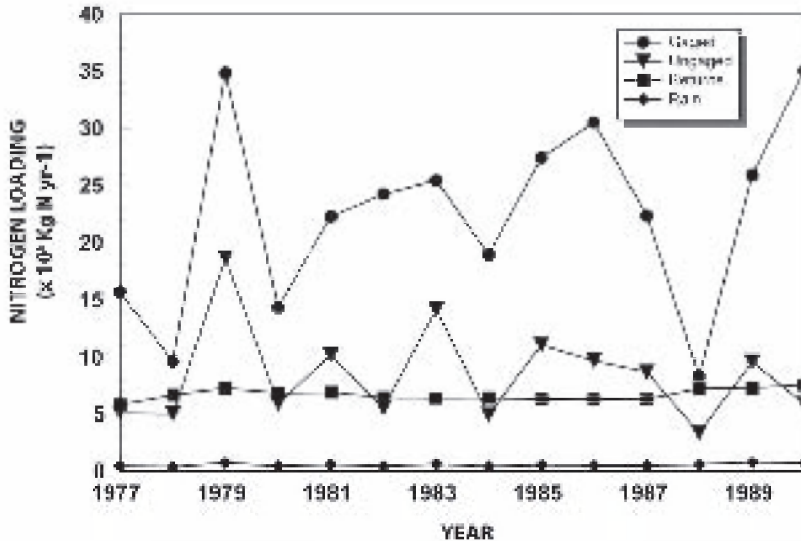

Figure 3. Annual estimates (1977-1990) of total nitrogen loading from 4 different sources for Galveston Bay. (Data from Stanley 2001).

of 0.633 ± 0.190 sd x 10^3 kg N km^{-2} y^{-1}. In comparison with four other large Texas estuaries, Galveston Bay received more than double the next highest area-specific N loading (Brock 2001). Atmospheric deposition of N directly to the estuary surface accounted for only 1.4% of the total N loading.

Using data from the National Atmospheric Deposition Program (NADP) for the period 1985 - 1996, Meyers *et al.* (2001) determined the total annual N deposition to the Galveston Bay watershed, which includes the open areas of the bay. The average annual loading rates (in kg N km^{-2} y^{-1}) were 0.0209 for wet deposition NH_4, 0.0188 for wet deposition NO_3, 0.0497 for wet deposition total N ($NH_4 + NO_3 + DON$), 0.0033 for dry deposition NH_4, 0.0328 for dry deposition NO_3, and 0.0394 for dry deposition total N (Meyers *et al.* 2001). Therefore the total estimated atmospheric nitrogen deposition (wet and dry) to Galveston Bay was 0.089 kg N km^{-2} y^{-1}.

Monthly N loading

D. Brock (Texas Water Development Board, Bays and Estuaries Program, Austin, Texas) graciously supplied monthly estimates of total N loading for Galveston Bay from 1977 to 1990 based upon modeling methods outlined in Brock *et al.* (1996). Monthly N loading events, like annual loading, was highly variable in both duration and magnitude (Figure 4). However, N loading was usually higher in the late winter-early spring months. The years 1989 and 1990 were 'wet' years with protracted river runoff and, consequently, high N loading rates. The higher resolution monthly rate
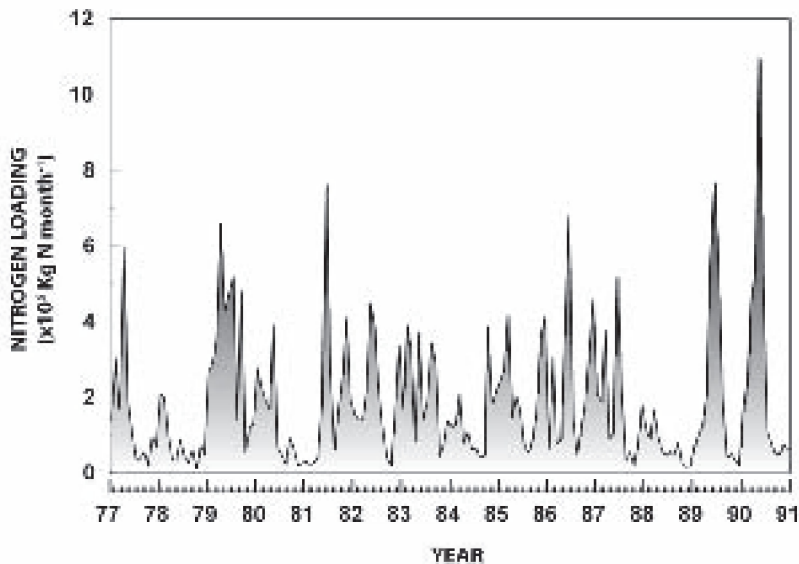

Figure 4. Monthly estimates (1977-1990) of total nitrogen loading for Galveston Bay. (Data courtesy of D. Brock, Texas Water Development Board).

estimates provide a mean annual loading estimate of $22,559 \pm 8,368$ sd x 10^3 kg N y^{-1}, which is much lower (59%) than the annual estimate given in Brock (2001). This discrepancy is attributed to the shorter-term averaging (monthly) which incorporates month to month variations in loading rates.

Benthic fluxes

Zimmerman and Benner (1994) undertook a study of denitrification, nutrient regeneration, and carbon mineralization in sediments collected from 5 stations in Galveston Bay. Denitrification rates, based on laboratory incubations of sediment cores, ranged from 0 to 47 μmol N_2 m^{-2} h^{-1} at temperatures ranging from 16.0 to 29.5°C. Summer (July) denitrification rates were the highest (30.2 μmol N_2 m^{-2} h^{-1}), followed by May (19.8) and March (5.4). Fluxes of nitrate + nitrite were from the sediment to the water (0 to 0.93 μmol N m^{-2} h^{-1}) at the lower estuary sites and from the water to the sediment (-0.21 to -1.21 μmol N m^{-2} h^{-1}) in the upper estuary. Ammonium fluxes (-0.29 to 3.21 μmol N m^{-2} h^{-1}) were highest in March and nearly always out of the sediments. Phosphate fluxes were small (<4 μmol P m^{-2} h^{-1}) and usually from the sediment to the overlying water. Overall, denitrification was responsible for ca. 75% of the benthic inorganic nitrogen flux in the spring and summer. In the winter, the majority (80%) of the nitrogen flux was in the form of ammonium. In the upper estuary, 24% of the N_2 production could be supported by the nitrate+nitrite influx into sediments and only 7% could be supported in the lower estuary. Thus the influx of water column nitrate and nitrite could not support the measured denitrification rates and illustrated a strong coupling of nitrification and denitrification in these sediments. Elemental analysis of pre- and post-incubation sediments showed preferential remineralization of nitrogen relative to carbon. Based on these measurements, Zimmerman and Benner (1994) estimated that denitrifiers were responsible for 37% of the total benthic carbon remineralization in the upper bay and 13% in the lower estuary and they attributed nearly one-third of the total sediment oxygen consumption to nitrification in this estuary. Overall, they estimated that denitrification removed only 14% of the total N loading into Galveston Bay.

Joye and An (1999) undertook a comprehensive 3-year study of denitrification at four locations in Galveston Bay. The average dentrification rate was 1.80 mmol N m^{-2} d^{-1} and ranged from 0.00 to 4.58, with lower rates in the winter and higher rates in the summer. The NO_3 flux into sediments supported, on average, 25% of the measured denitrification and suggested that the main source of NO_3 was from *in situ* nitrification. By extrapolating denitrification rates across the estuary, Joye and An (1999) estimated that the annual denitrification rate in Galveston Bay was 8.3 x 10^7 mol N month^{-1} and N removal via denitrification averaged 52% of the total N-loading.

In a similar study in Trinity Bay, An and Joye (2001) used light and dark *in situ* benthic chambers to measure the diel variability in sediment oxygen demand and the flux of N_2. Winter N_2 fluxes (in mmol m^{-2} d^{-1}) were 1.00 (light) and 0.48 (dark) while summer rates were 2.2 (light) and 0.1 (dark). Ammonium fluxes (mmol N m^{-2} d^{-1}) were 0.00 (winter) and 0.82 (summer) while nitrate fluxes were -0.1 (winter)

and 0.2 (summer). The daily rates for denitrification (mmol N m^{-2} d^{-1}) were 0.58 ± 0.04 sd for winter and 1.93 ± 0.1 sd for summer. These denitrification rates are four times larger than the rates reported by Zimmerman and Benner (1994). An and Joye (2001) attribute the disparity to the fact that their samples were incubated in both light and dark conditions while Zimmerman and Benner (1994) incubated their samples under dark conditions only. An and Joye (2001) found that denitrification rates were higher during the day and proposed that the higher rates were due to oxygen production by benthic microalgae, which enhanced the coupling between nitrification and denitrification. Using a simple model, An and Joye (2001) showed that when photosynthesis was inhibited, the rates of nitrification and denitrification decreased significantly. Based on the results of their study and modeling efforts, An and Joye (2001) estimated that more than 50% of the N load to the estuary is denitrified as compared to the estimate of 14% by Zimmerman and Benner (1994).

The findings of An and Joye (2001) highlight the importance of mixing events and turbulence on benthic/pelagic exchange of nutrients in Galveston Bay. During periods when sediments are resuspended, the overall effect is a reduction in the amount of light available for benthic microalgal photosynthesis. Thus denitrification rates would be slowed and the primary source of inorganic N would be NH_4 rather than NO_3. During calm weather periods, when turbidity is low, benthic microalgal photosynthesis may enhance the rates of nitrification-denitrification and reduce the input of dissolved inorganic nitrogen from sediments into overlying waters.

Warnken et al. (2000) undertook a study of benthic nutrient exchange in Trinity Bay from 1994 to 1996. Using both benthic chambers and porewater nutrient profiles, Warnken et al. (2000) calculated benthic and diffusive fluxes across the sediment water interface. Phosphate fluxes ranged from 0.08 to –0.53 mmol P m^{-2} d^{-1} while ammonium fluxes were always directed out of the sediments and ranged from –0.44 to –5.1 mmol N m^{-2} d^{-1}. Silicate fluxes were almost always out of the sediment and ranged from 1.7 to –1.2 mmol Si m^{-2} d^{-1}. A comparison of the rates and magnitudes of nutrient fluxes revealed that both direct measurements and diffusive flux methods agreed on the direction of fluxes, but differed in the magnitude. The diffusive flux method, based on porewater nutrient profiles, underestimated nutrient exchange rates relative to those determined by benthic chamber measurements. During the study period, turnover times for phosphate, silicate, and ammonium were 7-135 d, 4-56 d, and 0.3-10 d, respectively. These turnover times were significantly shorter than the average water residence time (1.5 yr.) for Trinity Bay during the study period. Benthic nutrient inputs of ammonium and phosphate were 1 to 2 orders of magnitude higher than inputs from the Trinity River and suggested that benthic regeneration was the primary source of these nutrients (NH_4 and PO_4) for Trinity Bay. Warnken et al. (2000) also found that benthic nutrient inputs were higher in the middle and outer regions of Trinity Bay. Elemental analysis of sediments showed lower C: N ratios for these areas and, therefore, suggested that the deposited autochthonous organic matter was of higher quality than other areas of the bay.

In May 1999, a biweekly sampling program was instituted to collect data on water quality, nutrient concentrations, and phytoplankton dynamics in Galveston and Trinity Bays. Samples for physical, chemical, and biological parameters were undertaken at biweekly to monthly intervals over a 33-month period (1999-2002) in Trinity Bay and Galveston Bay (Figure 1). The purpose of this program was to characterize short (monthly) to long-term (annual) changes in environmental variables, nutrients, and phytoplankton community structure and function.

Materials and methods

Eight to ten sampling stations were located along the long axis of Galveston Bay (Figure 1). Sampling at the stations consisted of vertical profiles of physical and chemical (O_2, pH, temperature, salinity, conductivity) parameters using a Hydrolab H20 water quality monitor. Irradiance (PAR) in the water column was determined using a LiCor 4π quantum sensor. The upper meter of the water column was sampled with a 1 m integrated water sampler (opaque PVC baler) and transported to a field laboratory for sample processing and preservation. Phytoplankton biomass, community composition and nutrient concentrations were determined for each sample. For nutrient analyses, water samples were filtered through combusted (350 °C, 2.5 h) Whatman GF/F (25 mm) filters, poured into acid-rinsed Nalgene bottles and stored at −20 °C until analyzed. Nitrate, nitrite, urea, phosphate and silicate were quantified according to Atlas *et al.* (1971) and ammonium was quantified according to Harwood and Kuhn (1970).

High performance liquid chromatography (HPLC) was used to determine chemosystematic photosynthetic pigments to estimate phytoplankton abundance. Aliquots (0.5 L) of seawater were filtered under a gentle vacuum (<50 kPa) onto 2.5 cm dia. glass fiber filters (Whatman GF/F), immediately frozen, and stored at −80 °C. For analyses, frozen filters were placed in 100 % acetone (1 ml), sonicated, and extracted at −20 °C for 18-20 h. Filtered extracts (375 µL) were injected into a Shimadzu HPLC equipped with a monomeric (Rainin Microsorb-MV, 0.46 x 10 cm, 3 µm) and a polymeric (Vydac 201TP, 0.46 x 25 cm, 5 µm) reverse-phase C_{18} column in series. A nonlinear binary gradient was used for pigment separations (Pinckney *et al.*, 1996). Absorption spectra and chromatograms (440 nm) were acquired using a Shimadzu SPD-M10av photodiode array detector. Pigment peaks were identified by comparison of retention times and absorption spectra with pure standards, including chlorophylls *a*, *b*, β-carotene, fucoxanthin, lutein, canthaxanthin, echinenone, gyroxanthin, peridinin, alloxanthin, and zeaxanthin (DHI, Denmark). Other pigments were identified by comparison to extracts from phytoplankton cultures and quantified using the appropriate extinction coefficients (Jeffrey *et al.* 1997). Detailed protocols for the HPLC photopigment methods are posted at http: //www.biol.sc.edu/~jpinckney/lab_protocols.htm.

Results

The Trinity River is the primary source of freshwater and new nutrient inputs into Trinity Bay and Galveston Bay (Figure 5). From May 1999 to February 2002, river discharge (x 10^7 m^3 d^{-1}) ranged from 224.3 to 1.8 with a mean flow of 24.9 (Figure 5). Peak discharge occurred in June 2001 and was associated with tropical storm Allison, which dropped ca. 94 cm of rain on the watershed over a 5 day period (National Weather Service, unpubl. data). Dry years (1999 and 2000) resulted in low river discharge and 2001 was already a relatively wet year prior to the arrival of the tropical storm. The low river discharge in 1999 and 2000 resulted in high salinities in excess of 25 psu in upper Trinity Bay (Figure 5). Likewise, high discharge in 2001 displaced isohalines towards the mouth of Galveston Bay and the tropical storm lowered salinities to < 5 psu over much of the bay. Bay salinities closely tracked freshwater discharge from the Trinity River. The diffuse attenuation coefficient (k_d) ranged from <1 to >10 m^{-1} with a mean of 2.28 ± 1.68 sd (Figure 5). Water clarity was generally lower during periods of high river discharge. Resuspension of sediments during moderate wind events (5-10 m sec^{-1}) was a major contributor to turbidity and light attenuation in the water column. Using an average k_d value of 2.28 m^{-1}, the depth of the 1% light level (the theoretical limit for net photosynthesis) would be 2.02 m. Since the average depth of Galveston Bay is 2.4 m, it is likely that benthic microalgal photosynthesis was frequently light-limited, especially in Trinity Bay. Phytoplankton chlorophyll a (Chl a) averaged 10.4 ± 10.1 sd µg L^{-1} and ranged from 0.27 to 101.5 µg Chl a L^{-1} over the study period (Figure 5). Phytoplankton blooms were associated with periods of moderate to high river discharge and the largest bloom, composed primarily of the dinoflagellate *Prorocentrum minimum*, occurred in February 2001. The red tide dinoflagellate, *Karenia brevis*, was advected into Galveston Bay from coastal waters in September 2000 and a moderate bloom (28.3 µg Chl a L^{-1}) was detected in the lower bay.

High river discharge events, especially in 2001, resulted in high concentrations of nitrite (NO_2) and nitrate (NO_3) in Trinity and Galveston Bays (Figure 6). For a period of ca. 4 months, NO_3 levels were > 30 µmol N L^{-1} over much of the upper bay. The passage of tropical storm Allison (June 2001), and associated high runoff and flushing, reduced NO_3 concentrations to less than 5 µmol N L^{-1} within a few days. In general, NO_2 concentrations were higher in the lower bay while NO_3 was higher in the upper bay and was directly linked to river discharge, suggesting that the Trinity River was the primary source of NO_3. Occasionally, ammonium (NH_4) concentrations exceeded 14 µmol N L^{-1}, but these occurrences were limited to short durations at isolated stations in the bay and were not associated with hypoxic/anoxic events. In December 2001 and June 2002, NH_4 concentrations were generally high (> 2 µmol N L^{-1}) throughout the bay (Figure 6). Although some NH_4 inputs appear to be associated with the Trinity River (only during times of high discharge), there are other times when high NH_4 concentrations do not seem to be related to river flow (e.g., summer 2001). The high NH_4 concentrations in March-May 2000 occurred when concentrations of NO_3 were low and may be indicative of spring runoff from newly fertilized croplands in the watershed. The high NH_4 concentrations in the middle and
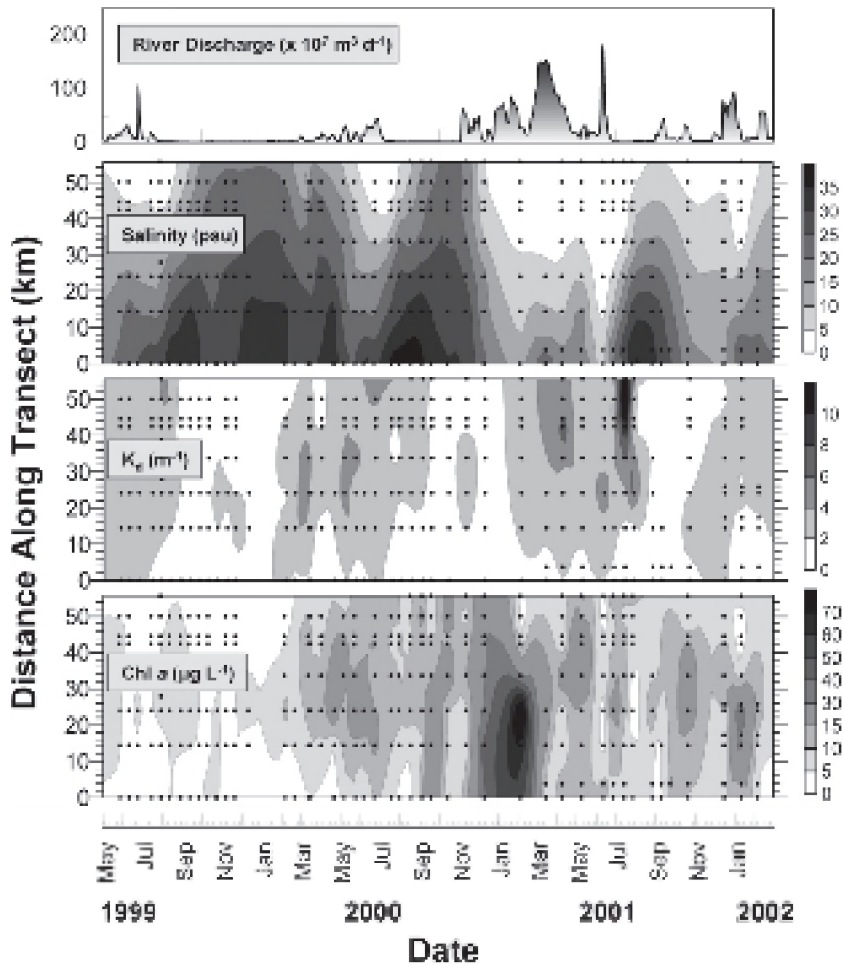
Figure 5. Spatio-temporal contour plots of salinity, diffuse attenuation coefficient, and chlorophyll *a* for Galveston Bay (1999-2002). The distance along transect refers to the distances given in Figure 1. The dots depict sampling dates and locations.

lower reaches of the bay may be attributable to benthic regeneration. The pattern for overall dissolved inorganic nitrogen (DIN = NO_2 + NO_3 + NH_4) was that concentrations were low from 1999 to mid-2000, then increased due to freshwater inflow from the Trinity River (Figure 6). Tropical storm Allison and associated heavy rainfall released a large amount of freshwater low in DIN (due to dilution) into Galveston Bay. By November 2001, the normal pattern of riverine DIN inputs resumed. The periods of high DIN concentrations were also correlated with phytoplankton biomass in the bay and indicates the tight coupling between DIN inputs and phytoplankton responses (Figs. 5, 6).
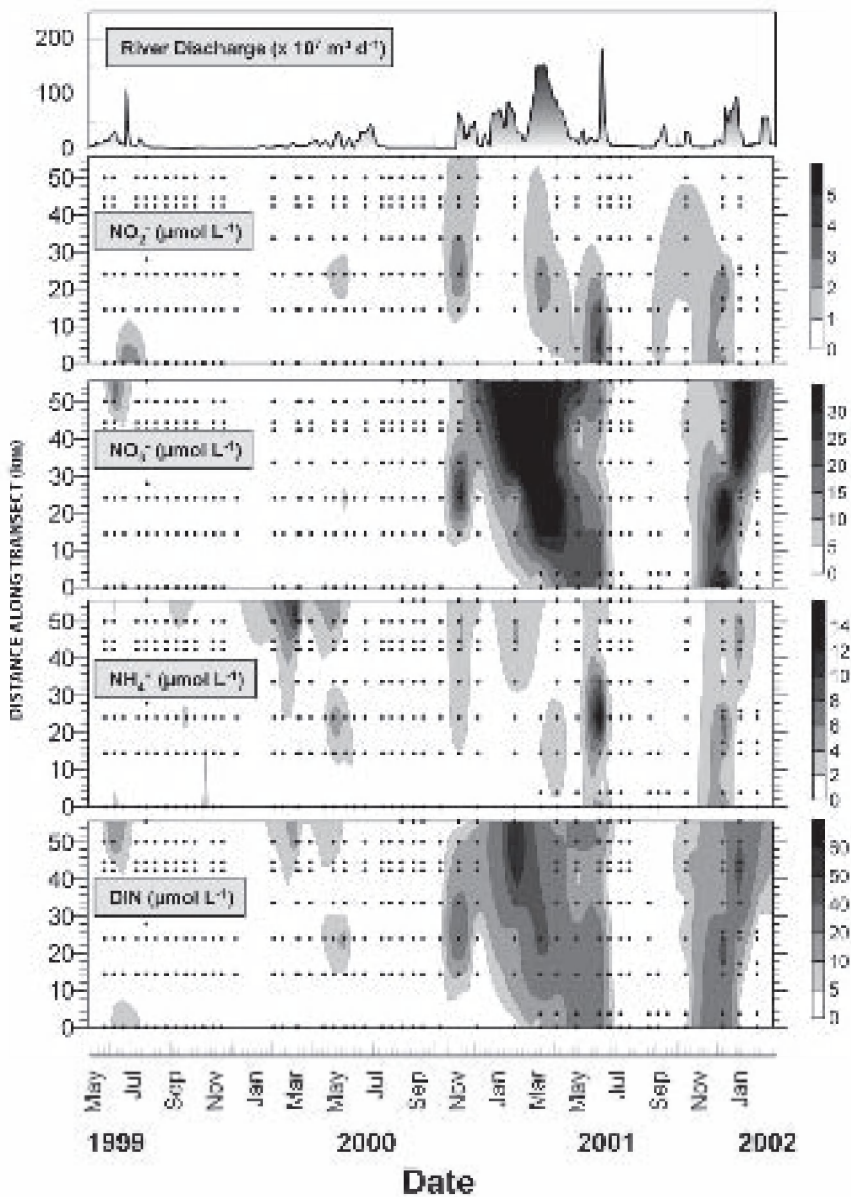
Figure 6. Spatio-temporal contour plots of nitrite, nitrate, ammonium, and total dissolved inorganic nitrogen for Galveston Bay (1999-2002). The distance along transect refers to the distances given in Figure 1. The dots depict sampling dates and locations.

Urea concentrations were generally low (< 2 µmol N L^{-1}) but reached a high of 30.3 µmol N L^{-1} in the lower bay in June 2001, following tropical storm Allison (Figure 7). Phosphate (PO_4) concentrations averaged 3.23 ± 2.38sd µmol P L^{-1} and ranged from 0 to 14.5 (Figure 7). Concentrations were generally higher in the summer months in the upper bay, with the exception of January 2002 when high PO_4 levels were detected in the lower bay. In general, PO_4 showed an inverse relationship with river discharge, suggesting that the major source of PO_4 may be benthic regeneration. The mean silicate ($SiOH_4$) concentration over the study period was 42.2 $\pm$ 30.2 sd µmol Si L^{-1} and ranged from 1.66 to 161 (Figure 7). Like PO_4, silicate concentrations were highest under low river flow conditions in Trinity Bay. The low concentrations may reflect utilization by diatoms when DIN concentrations were high. Alternatively, higher concentrations of silicate may be due to benthic regeneration during the warm summer months. Silicate concentrations peaked after the passage of tropical storm Allison and may indicate the input of silicate (as sediment) in stormwater runoff or possibly sediment turnover following the storm.

The DIN: P molar ratio averaged 3.55 ± 7.51 sd and ranged from 0.01 to 80.5. A plot of the paired DIN and P values shows that this ratio was rarely above the Redfield ratio of 16: 1 and suggests that phytoplankton in Galveston Bay were usually N-limited (Figure 8). In February and June 2001, the ratio exceeded 16: 1 due to the high concentrations of nitrate associated with riverine N loading. During these brief events, phytoplankton in the bay may have been P-limited.

Discussion

Freshwater discharge from the Trinity River into Galveston Bay plays a major role in the fluctuations of salinity, nutrients, and phytoplankton biomass. During periods of high river flow, nitrate is the major form of inorganic N added to the estuary and is a source of *new* N for the system. When river flows are low, especially during dry summer months, the bay receives little N input from the river and the major source of N must be through regeneration, either from the benthos or the water column. During these periods, benthic remineralization and release is a likely source for DIN (Zimmerman and Benner 1994; Joye and An 1999; Warnken *et al.* 2000). However, phytoplankton uptake of DIN may prevent measurable accumulations of DIN in the water column. Spring inputs of ammonium from the Trinity river are likely due to agricultural runoff, since this is the time of year when farmers fertilize their fields with ammonium or urea-based fertilizers. Warnken *et al.* (2000) reported benthic ammonium fluxes as high as 5.1 mmol N m^{-2} d^{-1} while An and Joye (2001) found rates of 0.82 mmol N m^{-2} d^{-1} in Galveston Bay during the summer months. Therefore, ammonium regeneration from the benthos is likely a consistent source of N for the estuary. During dry periods, benthic release of ammonium is probably the primary source of N for phytoplankton in the bay.

The primary source of phosphate for the bay seemed to be benthic regeneration. The highest phosphate concentrations occurred during low river flow in the summer months. Additionally, phosphate concentrations were lowest during high river discharge
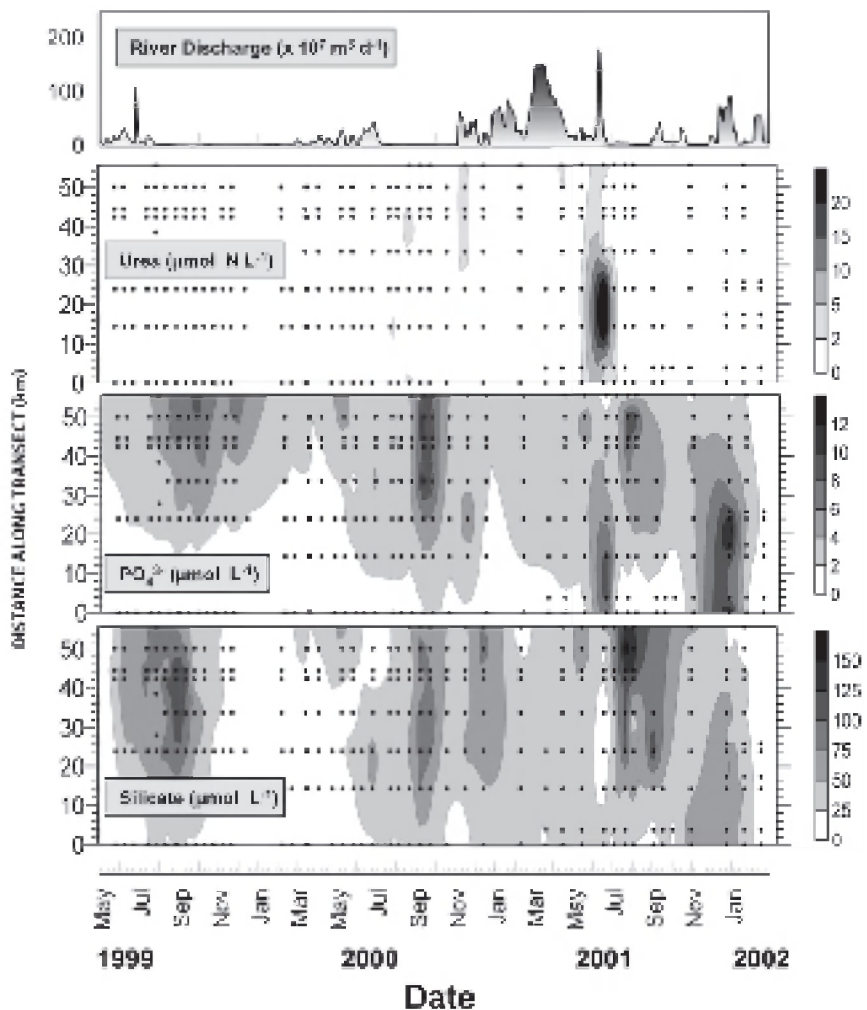
Figure 7. Spatio-temporal contour plots of urea, phosphate, and silicate for Galveston Bay (1999-2002). The distance along transect refers to the distances given in Figure 1. The dots depict sampling dates and locations.
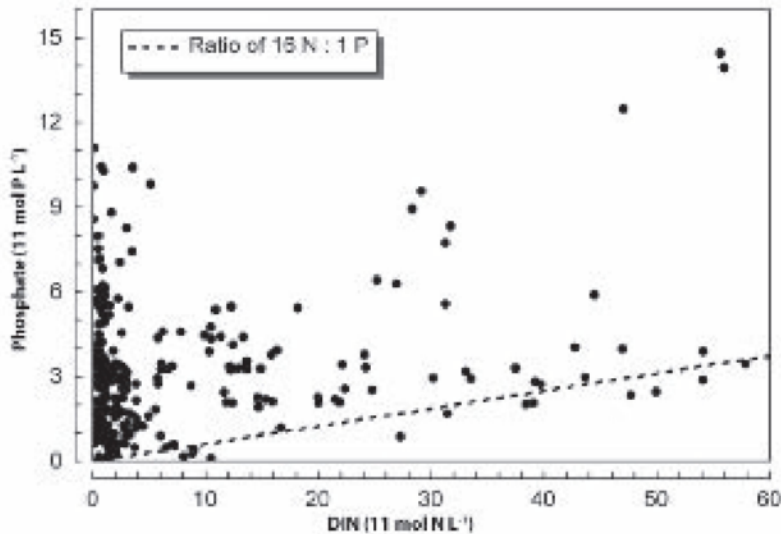
Figure 8. Plot of phosphate vs. total dissolved inorganic nitrogen for individual samples taken from Galveston Bay (1999-2002). The dashed line represents the Redfield ratio of 16 N : 1 P. Points above the line indicate N-limitation and values below the line suggest P-limitation for phytoplankton.

conditions. Upon examination of a 9-year data set, Santschi (1995) reported that phosphate concentrations regularly reach a maximum in September. The data in the present study reflect this observation exactly. Zimmerman and Benner (1994) report small phosphate fluxes of < 4 µmol P h^{-1}, but their study was conducted from March through July, missing the period when P release was usually highest. Warnken et $al.$ (2000) found P flux rates as high as 0.53 mmol m^{-2} d^{-1} in Galveston Bay. The inverse relationship between river discharge and phosphate concentration could be due simply to dilution. However, during high flow conditions with high nitrate concentrations, the phytoplankton demand for P would be higher than under low N conditions. Thus the fluctuations in phosphate concentrations were likely a dynamic balance between benthic regeneration and phytoplankton uptake. Silicate concentrations closely tracked phosphate and similar regulating mechanisms may apply to this nutrient as well.

Urea and nitrite were usually minor nutrients Galveston Bay, except following the passage of tropical storm Allison. High concentrations were measured in the lower bay along the deep ship channel. Tropical storm Allison was an important event in the biogeochemistry of Galveston Bay. Following the passage of the storm, ammonium, urea, and phosphate concentrations briefly increased by an order of magnitude in lower Galveston Bay (Figs. 6, 7). These high nutrient concentrations suggest there was significant remineralization of organic matter, possibly particulate organic matter washed downstream following the storm (Paerl et $al.$ 1998). With further flushing of the system by freshwater input, DIN concentrations were reduced to low levels (total

DIN < 5 μmol L^{-1}), probably due to dilution by high rainfall and rapid runoff associated with the tropical storm. Thus the tropical storm 'flushed' the system of dissolved nutrients. The bay seems to have recovered within 3-4 months after storm passage, with moderate concentrations of DIN resulting from late winter rains and river discharge.

Phytoplankton blooms closely tracked nitrate concentrations in Galveston Bay, although peaks in biomass were displaced downstream from peaks in nitrate concentration. The lower salinity (< 10 psu) in the upper bay during these periods may have prevented the formation of large blooms. Blooms likely formed as the DIN was mixed with higher salinity waters in the lower bay. Twelve nutrient (NO_3^-, PO_4^{3-}) addition bioassays, conducted from May 1999 to July 2000, indicated that the phytoplankton community in Galveston Bay was consistently N-limited (Örnòlfsdòttir 2002). All major algal groups of the community showed significant increases in biomass in response to the addition of NO_3^- (10 μM final concentration), sometimes resulting in a doubling in biomass (relative to controls) over a 24 hour incubation period. Evidence of phosphate or silicate limitation was not detected in these bioassays. In terms of size distributions, the picoplankton (< 2 μm), nanoplankton (2-20 μm), and microplankton (20-200 μm) fractions constituted 18%, 50%, and 32% of the total community biomass, respectively. All size ranges had representatives from most of the major algal groups and the nanoplankton had the highest diversity. The DIN: P ratio for Galveston Bay further supports the finding of N-limitation for phytoplankton. Over much of the 3-year study period, the DIN: P ratio was <16, the critical value according to the Redfield ratio. On the few occasions when the ratio was >16, the P limitation was likely the result of high DIN loading.

The ability of phytoplankton to take advantage of high nutrient conditions is also influenced by turbidity, which results in light limitation. Moderate winds that blow over bay waters resuspend sediments in the shallow bay waters. The average diffuse attenuation coefficient (k_d) over the 3-year period was 2.28 m^{-1}, which translates into a light level of 1% of incoming irradiance at a depth of 2.02 m. Thus, on average, benthic microalgal productivity is likely very low in waters deeper than 2 m. With an average bay depth 2.4 m, much of the benthos (and benthic microalgae) was usually light-limited. The shallow water column in Galveston Bay is usually well-mixed and phytoplankton may be able to sustain photosynthesis due to vertical mixing processes. Therefore, one could speculate that most of the primary production in Galveston Bay can be attributed to phytoplankton rather than benthic microalgae, especially during turbid conditions. Furthermore, benthic microalgal biomass in the bay is less than 10 mg Chl a m^{-2} (Pinckney and Lee, *in prep.*), which roughly approximates the areal biomass of phytoplankton.

Summary

This review has focused on the spatial and temporal scales of nutrient fluctuations in Galveston Bay, a large shallow subtropical estuary typical of the Gulf of Mexico.

Decadal and annual estimates of total N loading highlight the importance of interannual variation and long-term trends, which are useful for developing nutrient input management strategies and assessing the effectiveness of mitigation programs. However, long-term averaging of large spatial areas dampens the frequency and magnitude of seasonal events and system perturbations. Monthly estimates of N loading capture some of this variability and illustrate that monthly variation is higher (in relative terms) than annual variations. The comparison of Brock's (2001) loading estimates based on annual averaging (38,350 x 10^3 kg N y^{-1}) and monthly averaging (22,559 x 10^3 kg N y^{-1}) for the same time period (1977 - 1990) shows that the temporal averaging scale makes a big difference when estimating loading. Ideally, the best temporal scale for estimating loading rates is the frequency at which loading events occur to the system. In the case of Galveston Bay, major N loading events are directly related to Trinity River discharge. Since discharge is a function of meteorological conditions, which are unpredictable at time scales > 2 weeks, water samples for the determination of nutrient concentrations (to calculate loading) should be collected daily to obtain accurate and reliable loading estimates. Unfortunately, this sampling frequency is unreasonable for most monitoring agencies. The further development and implementation of *in situ* nutrient analyzers may provide the resolution needed for real-time, cost-effective estimates of nitrate loading.

The dynamic nature of nutrient distributions in Galveston Bay is clearly illustrated in the spatio-temporal contour plots. Nutrient concentrations in this estuary reflected a balance between river discharge, benthic regeneration, and water temperature (season). Major perturbations, such as the passage of tropical storm Allison, upset this balance and profoundly changed the biogeochemistry of the estuary. After this 'flushing' event, the system seemed to slowly return to a 'normal' pattern of nutrient distributions. High-resolution contour plots provided useful insights into the spatio-temporal relationships between different nutrients and the causal mechanisms responsible for the observed distributions.

Biotic responses to nutrient inputs were rapid, on time scales of 1 day. Estuarine phytoplankton biomass quickly increased, taking advantage of higher nutrient concentrations. In Galveston Bay, the phytoplankton community was N-limited and showed nearly instantaneous increases in biomass when DIN (primarily NO_3) was loaded into the estuary. Thus nutrient fluctuations on daily time scales can have profound effects on primary productivity in this estuary. In addition, the timing of loading events may also play a role in determining phytoplankton community structure. For example, short-term pulses of high NO_3 loading may favor diatoms while long periods of low loading could promote growth of smaller phytoplankton and phytoflagellates (Huisman and Weissing 1995).

Although atmospheric inputs of N are small (1.4% of total N loading) for Galveston Bay, this input could be very important, especially during periods of low river discharge. Afternoon showers during the summer could provide a significant source of *new* N to the estuary. Benthic fluxes of nutrients provide a nearly constant (depending on season) source of nutrients for phytoplankton. Again, during periods of low river discharge, the benthic flux is responsible for sustaining phytoplankton productivity. Denitrification appears to be the largest N sink for this estuary. Although there

is disagreement on the actual rates, denitrification is responsible for removing from 14 % to 52 % of the total N loading. Of course, this estimate will change depending on the actual loading for the estuary.

Documenting nutrient fluctuations in estuaries is relatively straightforward provided the funding, time, and resources are available. Understanding the relative importance of the different processes driving these fluctuations on a system scale is a much more formidable task. Mechanistic studies of benthic and planktonic biogeochemical processes, coupled in space in time, are a necessary prerequisite for developing reliable models to simulate, and possibly predict, estuarine nutrient fluctuations.

Acknowledgements

References

AHNER, B.A., MOREL, F.M.M., and MOFFETT, J.W. 1997. Trace metal control of phytoplankton production in coastal waters. Limnol. Oceanogr. **42**: 601-608.

ALONGI, D.M. 1998. Coastal ecosystem processes. CRC Press.

AMON, R.M.W., and R. BENNER. 1994. Rapid cycling of high-molecular-weight dissolved organic matter in the ocean. Nature **369**: 549-552.

AN, S., and S.B. JOYE. 2001. Enhancement of coupled nitrification-denitrification by benthic photosynthesis in shallow estuarine sediments. Limnol. Oceanogr. **46**: 62-74.

ATLAS, E.L., S.W. HAGER, L.I. GORDON. and P.K. PARK. 1971. A practical manual for use of the Technicon AutoAnalyzer in seawater nutrient analyses; revised. Oregon State University, Corvallis, Technical Report 215.

AZAM, F., T. FENCHEL, G.J. FIELD, J.S. GRAY, L.A. MEYER-REIL, and F. THINGSTAD. 1983. The ecological role of water-column microbes in the sea. Mar. Ecol. Prog. Ser. **10**: 257-263.

AZAM, F., D.C. SMITH, G.F. STEWARD, and A. HAGSTROM. 1993. Bacteria-organic matter coupling and its significance for oceanic carbon cycling. Microb. Ecol. **28**: 167-179.

BENNETT, M.E., and J.E. HOBBIE. 1972. The uptake of glucose by *Chlamydomonas* sp. J. Phycol. **8**: 392-398.

BRICKER, S.B., C.G. CLEMENT, D.E. PIRHALLA, S.P. ORLANDO, D.R.G. FARROW. 1999. National estuarine eutrophication assessment: Effects of nutrient enrichment on the Nation's estuaries. National Oceanic and Atmospheric Administration, Washington, D.C.

Brock, D.A. 2001. Uncertainties in individual estuary N-loading assessments. p. 171-185. *In* R.A. Valigura *et al.* [eds.], Nitrogen loading in coastal waterbodies: An atmospheric perspective. Coastal and Estuarine Studies 57. American Geophysical Union, Washington, DC.

BROCK, D.A., R.S. SOLIS, and W.L. LONGLEY. 1996. Guidelines for water resources permitting: Nutrient requirements for maintenance of Galveston Bay Productivity. Final Report to Near Coastal Waters Program, EPA. by Texas Water Development Board, Austin, TX. 131 pp.

BURTON, J. D., and P.S. LISS. 1976. Estuarine chemistry, Academic Press.

CAPONE, D.G. 2000. The marine microbial nitrogen cycle, p. 455-493. *In* D.L. Kirchman [ed.], Microbial ecology of the oceans. Wiley-Liss, Inc.

CARLSSON, P., H. EDLING, and C. BECHEMIN. 1998. Interactions between a marine dinoflagellate (*Alexandrium catanella*) and a bacterial community utilizing riverine humic substances. Aquat. Microb. Ecol. **16**: 65-80.

CRINER, O., and M.D. JOHNICAN. 2002. Update 2000: Current status and historical trends of the environmental health of Galveston Bay. Galveston Bay Estuary Program. Webster, Texas.

CROCKER, P.A., and P.C. KOSKA. 1996. Trends in water and sediment quality for the Houston Ship Channel. Texas J. Sci. **48**: 267-282.

CROOT, P.L., J.W. MOFFETT, and L.E. BRAND. 2000. Production of extracellular Cu complexing ligands by eukaryotic phytoplankton in response to Cu stress. Limnol. Oceanogr. **45**: 619-627.

DAME, R., J. SPURRIER, and T. WOLAVER. 1989. Carbon, nitrogen, and phosphorus processing by an oyster reef. Mar. Ecol. Prog. Ser. **54**: 249-256.

DORTCH, Q. 1990. The interaction between ammonium and nitrate uptake by phytoplankton. Mar. Ecol. Progr. Ser. **61**: 183-201.

DROOP, M.R. 1974. Heterotrophy of carbon, p. 530-559. *In* W.D.P. Stewart [ed.]. Algal Physiology and biochemistry. Blackwell Sci.

FARRINGTON J.W. 1992. Marine organic geochemistry: review and challenges for the future. Mar. Chem. **39**: 1-244.

FISHER, T., E. PEELE, J. AMMERMAN, and L. HARDING. 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. Mar. Ecol. Prog. Ser. **82**: 51-63.

GAINES, G., and M. ELBRÄCHTER. 1987. Heterotrophic nutrition. p. 224-268. *In* F.J.R. Taylor [ed.], The biology of dinoflagellates. Blackwell Sci.

GLIBERT, P., D. CONLEY, T. FISHER, L. HARDING, and T. MALONE. 1995. Dynamics of the 1990 winter/spring bloom in Chesapeake Bay. Mar. Ecol. Prog. Ser. **122**: 27-43.

GUO, L., P.H. SANTSCHI, and T.S. BIANCHI. 1999. Dissolved organic matter in estuaries of the Gulf of Mexico. p. 269-299 *In*: T.S. Bianchi, J.R. Pennock, and R.R. Twilley [eds.]. Biogeochemistry of Gulf of Mexico estuaries. John Wiley and Sons.

HARWOOD, J.E., and A.L. KUHN. 1970. A colorimetric method for ammonia in natural waters. Water Res. **4**: 805-811.

HELLEBUST, J.A., and J. LEWIN. 1977. Heterotrophic nutrition, p. 169-197. *In* W. Werner [ed.]. The biology of diatoms. Blackwell Sci.

HOBBIE, J.E. [ed] 2000. Estuarine science: a synthetic approach to research and practice. Island Press. Pp. 593

HUISMAN, J. and F. WEISSING. 1995. Competition for nutrients and light in a mixed water column: a theoretical approach. Am. Nat. **146**: 536-564.

HUNG, C.C., D. TANG, K. WARNKEN, and P.H. SANTSCHI. 2001. Distributions of carbohydrates, including uronic acids, in estuarine waters of Galveston Bay. Mar. Chem. 73: 305-318.

JEFFREY, S., R. MANTOURA, and S. WRIGHT. [eds.]. 1997. Phytoplankton pigments in oceanography: Guidelines to modern methods. UNESCO.

JOYE, S.B., and S. AN. 1999. Denitrification in Galveston Bay Final Report. Submitted to Texas Water Development Board, Austin, Texas.

KEIL, R.G., and D.L. KIRCHMAN. 1994. Abiotic transformation of labile protein to refractory protein in sea water. Mar. Chem. **45**: 187-196.

KIEBER, D., J. MCDANIEL, and K. MOPPER. 1989. Photochemical source of biological substrates in seawater: Implications for carbon cycling. Nature **341**: 637-639.

KIRCHMAN, D.L., Y. SUZUKI, C. GARSIDE, and H.W. DUCKLOW. 1991. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. Nature **352**: 612-614.

LOWERY, T.A. 1998. Difference equation-based estuarine flushing model application to U.S. Gulf of Mexico estuaries. J. Coastal Res. **14**: 185-195.

MILLIMAN, J.D. 1974. Marine carbonates. Springer-Verlag. Pp. 374

MEYERS, T., J. SICKLES, R. DENNIS, K. RUSSELL, J. GALLOWAY, and T. CHURCH. 2001. Atmospheric nitrogen deposition to coastal estuaries and their watershed. p. 53-76. *In* R.A. Valigura *et al.* [eds.]. Nitrogen loading in coastal waterbodies: An Atmospheric perspective. Coastal and Estuarine Studies 57. American Geophysical Union.

MOFFETT, J.W., and L.E. BRAND. 1996. Production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. Limnol. Oceanogr. **41**: 388-395.

MORSE, J.W., B.J. PRESLEY, R.J. TAYLOR, G. BENOIT, and P. SANTSCHI. 1993. Trace metal chemistry of Galveston Bay: water, sediments and biota. Mar. Environ. Res. **36**: 1-37.

NEILSON, A.H. and R.A. LEWIN. 1974. The uptake and utilization of organic carbon by algae: an assay in comparative biochemistry. Phycologia **13**: 227-264.

NIXON, S. 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia **41**: 199-219.

NRC (National Research Council). 2000. Clean coastal waters: understanding and reducing the effects of nutrient pollution. National Academy Press.

NOAA (National Oceanic and Atmospheric Administration). 1989. Galveston Bay: Issues, resources, status, and management. NOAA Estuary of the Month Seminar Series No. 13. US Department of Commerce.

OGAWA, H., Y. AMAGAI, I. KOIKE, K. KAISER, and R. BENNER. 2001. Production of refractory dissolved organic matter by bacteria. Science **292**: 917-920.

ÖRNÓLFSDÓTTIR, E.B. 2002. The ecological role of small phytoplankton in phytoplankton production and community composition in Galveston Bay, Texas. Ph.D. Dissertation. Texas A&M University.

PAERL, H.W. 1990. Physiological ecology and regulation of N_2 fixation in natural waters. Adv. Microb. Ecol. **11**: 305-344.

PAERL, H.W. 1995. Coastal eutrophication in relation to atmospheric nitrogen deposition: current perspectives. Ophelia **41**: 237-259.

PAERL, H.W., J.L. PINCKNEY, J.M. FEAR, and B.L. PEIERLS. 1998. Ecosystem responses to internal and watershed organic matter loading: consequences for hypoxia in the eutrophying Neuse River estuary, North Carolina, USA. Mar. Ecol. Prog. Ser. **166**: 17-25.

PILSON, M.E.Q. 1998. An introduction to the chemistry of the sea. Prentice-Hall.

PINCKNEY, J., D. MILLIE, K. HOWE, H. PAERL, and J. HURLEY. 1996. Flow scintillation counting of ^{14}C-labeled microalgal photosynthetic pigments. J. Plankton Res. **18**: 1867-1880.

PROSPERO, J., K. BARRETT, T. CHURCH, F. DENTENER, R. DUCE, J. GALLOWAY, H. LEVY, J. MOODY, and P. QUIN. 1996. Atmospheric deposition of nutrients to the North Atlantic basin. Biogeochemistry **35**: 27-73.

ROBINSON, L., P. CAMPBELL, and L. BUTLER. 2000. Trends in commercial fishery landings, 1972-1988. Texas Parks and Wildlife Department, Coastal Fisheries Division, Austin, Texas.

SANTSCHI, P.H. 1995. Seasonality of nutrient concentrations in Galveston Bay. Mar. Environ. Res. **40**: 337-362.

SHARP, J. 1991. Review of carbon, nitrogen, and phosphorus biogeochemistry. Rev. Geophys. 1991: 648-657.

SHERR, E.B. 1988. Direct use of high molecular weight polysaccharide by heterotrophic flagellates. Nature **335**: 348-351.

STANLEY, D. 2001. An annotated summary of nitrogen loading to US estuaries. p. 227-252. *In* R.A. Valigura *et al.* [eds.]. Nitrogen loading in coastal waterbodies: An Atmospheric perspective. Coastal and Estuarine Studies 57. American Geophysical Union.

TANG, D., K.W. WARNKEN, and P.H. SANTSCHI. 2001. Organic complexation of copper in surface waters of Galveston Bay. Limnol. Oceanogr. **46**: 321-330.

TOBIAS, C.R., J.W. HARVEY, and I.C. ANDERSON. 2001. Quantifying groundwater discharge through fringing wetlands to estuaries: seasonal variability, methods comparison, and implications for wetland-estuary echange. Limnol. Oceanogr. **46**: 604-615.

WARD, B.B. and D.A. BRONK. 2001. Net nitrogen uptake and DON release in surface waters: importance of trophic interactions implied from size fractionation experiments. Mar. Ecol. Prog. Ser. **219**: 11-24.

WARNKEN, K.W., G.A. GILL, P.H. SANTSCHI, and L.L. GRIFFIN. 2000. Benthic exchange of nutrients in Galveston Bay, Texas. Estuaries **23**: 647-661.

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