Nutrient Dynamics

What is the relative importance of the advection of exogenous nutrients, internal nutrient cycling including exchange between water column and sedimentary nutrient sources, and nitrogen fixation in determining the nutrient budget for Florida Bay?

Contents

About this report

This report draws its material directly from syntheses compiled for the 2001 Florida Bay Science Conference. The Florida Bay Science Program organizes itself around five central research questions. Topical teams associated with each question consist of modelers and researchers working in the Bay and adjacent marine systems. These teams compiled the original synthesis documents.

In preparation for the 2003 Florida Bay Science Conference, the research teams have modified the existing synthesis documents to bring them up to date and implement a more uniform, common format. In some cases, entirely new documents have been drafted, such as the information here on ecosystem history and on nutrient dynamics. The present report compiles these separate documents into one and provides the reader with summary material as a guide to the contents.

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Introduction

Question 2: What is the relative importance of the influx of external nutrients and of internal nutrient cycling in determining the nutrient budget of Florida Bay? What mechanisms control the sources and sinks of the Bay's nutrients?

Ecological changes within Florida Bay, including *Thalassia testudinum* mass mortality and algal blooms, which have been evident during the last two decades, have commonly been attributed to many of the same human activities that have changed the Everglades. The diversion of freshwater to the Atlantic coast by canals has increased the salinity of the bay. Freshwater discharges from canals to the Atlantic Ocean were roughly four times larger than discharges to sloughs that flowed toward Florida Bay in the 1980s. Additionally, anthropogenic nutrient inputs from the Florida Keys, Gulf of Mexico, the atmosphere, and the Everglades may have increased. Inputs from The Gulf may include phosphorus that is transported by long-shore currents from the central Florida coast and nitrogen from the Everglades that flows into the Gulf from the Shark River Slough.

The main information needs relative to nutrient cycles in Florida Bay are an understanding of the factors that triggered and maintain the mass mortality of seagrasses and the episodic phytoplankton blooms. Also critical is sufficient understanding to enable us to assess the impact of various environmental management strategies being considered for Bay restoration. In particular, we need to accurately predict the sensitivity of the Bay's nutrient cycles to changing fresh water flow to the Bay, and the resultant change in the Bay's salinity regime. For much of the Bay, any factor that increases P availability either by increasing sources or decreasing removal is likely to exacerbate the current problems of the Bay. Recent evidence also indicates that algal blooms in the central and western Bay are sometimes stimulated by N enrichment. Thus we need thorough understanding of the Bay's nutrient cycles. Questions that the current monitoring and research program must address in order to meet these needs are as follows.

The water column in Florida Bay is generally oligotrophic, and historically phytoplankton biomass has been quite low throughout the system. Although phytoplankton in Florida Bay are generally phosphorous limited (Fourqurean et al 1993; Phlips and Badylak 1996; Lavrentyev et al. 1998), other resources (e.g. light, nitrogen, silicon) may also be important in controlling plankton biomass in some areas of the Bay (Lavrentyev et al. 1998). Dissolved inorganic phosphorous (DIP) concentrations are near detection limits (20 nM). While concentrations of dissolved inorganic nitrogen (DIN) can be relatively high (median value 3.3 µM, but concentrations > 10 µM are not uncommon) and dominated by ammonium (Fourqurean et al. 1993; Boyer et al. 1997) – as summarized in Fourqurean and Robblee (1999).

A spatial analysis of data from the FIU monitoring program resulted in the delineation of 3 groups of stations that have robust similarities in water quality (Fig. 5.1). We have argued that these spatially contiguous groups of stations are the result of similar hydrodynamic forcing and processing of materials; hence we call them 'zones of similar influence'. The Eastern Bay zone acts most like a 'conventional' estuary in that it has a quasi-longitudinal salinity gradient caused by the mixing of freshwater runoff with seawater. In contrast, the Central Bay is a hydrographically isolated area with low and infrequent terrestrial freshwater input, a long water residence time, and high evaporative potential. The Western Bay zone is the most influenced by the Gulf of Mexico tides and is also isolated from direct overland freshwater sources.

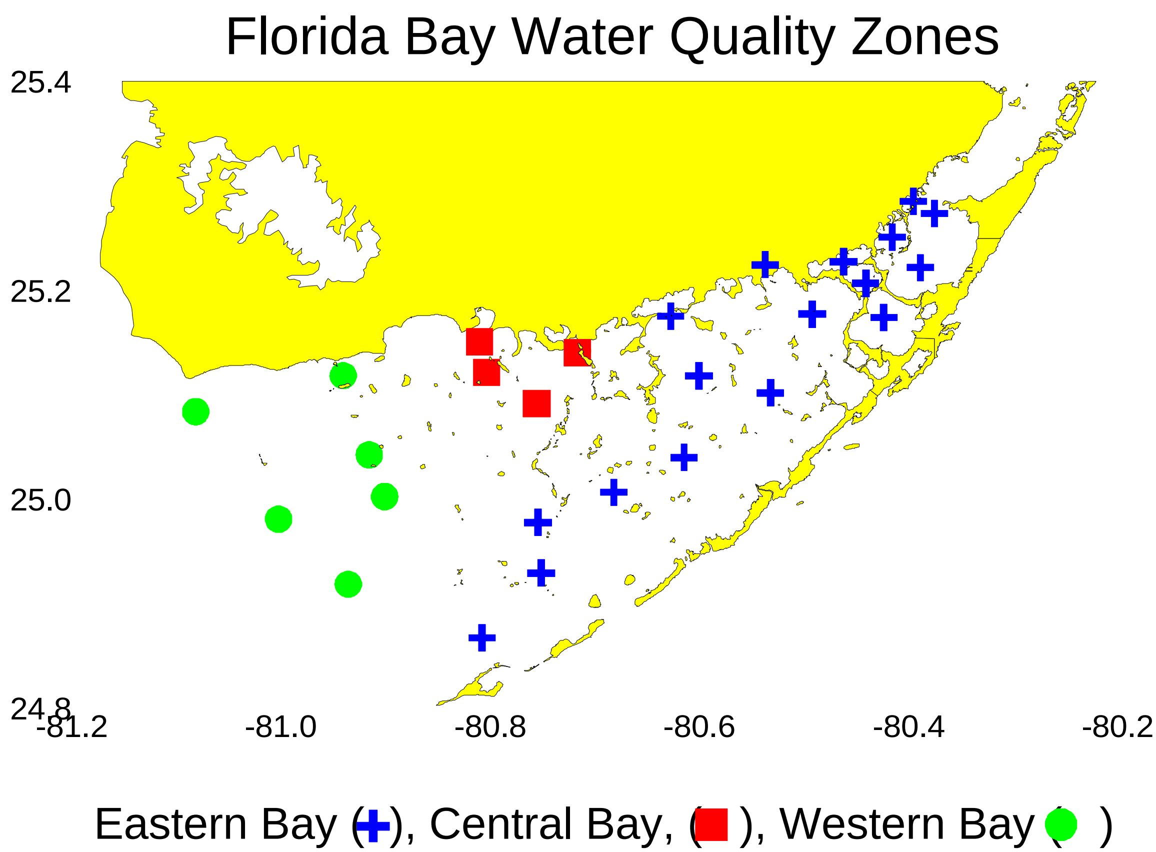

Figure 5.1: Zones of similar water quality in Florida Bay

Summary of Our State of Knowledge

Research on nutrient dynamics in Florida Bay focuses on the exchange with adjacent regions ("external" dynamics), the cycling of nutrients within Florida Bay ("internal" dynamics), and the influence of these processes on ecosystem structure and function, i.e. on spatial and temporal variation, Table 5.1. A continuing program of monitoring and research, including computer modeling, addresses the question of how human activity is affecting the nutrient dynamics of Florida Bay and how future restoration actions will alter these dynamics.

- <u>What do we know about status and trends in water quality over space and time?</u>
  - Objective analysis shows that there are three zones in the bay that exhibit significant differences in water quality characteristics due to nutrient inputs, tidal advection, and water residence time. These are the Eastern, Central, and Western bays.
  - In general, dissolved phosphorus concentrations increase and nitrogen decreases from east to west resulting in a shift from P limitation to N limitation.
  - Central Bay waters have high ammonium concentrations, which may indicate a bottleneck in the process of nitrification.
  - Temporal trends over a 13-year period of record show bayside declines in total phosphorus, total nitrogen, and chlorophyll *a* with an overall increase in turbidity.

- <u>What do we know about sources and amounts of external nutrient loading to Florida Bay?</u>
  - Terrestrial nutrient loading fluctuates with freshwater flow, however, flow-weighted concentrations decrease with increasing flow.
  - Phosphorus loading from the Everglades is a small proportion of the Florida Bay nutrient budget. Most P appears to be derived from the Gulf of Mexico.
  - Nitrogen output from the southern Everglades (including Shark River Slough) is a significant proportion of the Florida Bay nutrient budget (similar in magnitude to atmospheric loading). Most nitrogen flowing from the wetlands is in the form of dissolved organic compounds. Studies on the bioavailability of DON are currently underway.
  - The atmospheric input of nutrients is large and most atmospheric nitrogen is inorganic.
  - Knowledge of the Bay's nutrient budget is coarse over time and space (annual averaging for entire bay). Large uncertainty exists regarding the magnitude of nutrient exchange at the Gulf of Mexico boundary and regarding saline groundwater sources.
  - There is a measurable effect of water management on the quantity and distribution of water and nutrients through the length of the Taylor Slough / C111 basin system, influencing inputs to Florida Bay.
  - A serious disconnect exists between upland/canal loading estimates and actual input to the bay because of unmeasured nutrient processing in the intervening wetland/mangrove areas.

- <u>What do we know about internal nutrient cycling processes?</u>
  - Benthic denitrification is higher than expected based on denitrification/N-loading relationships in other estuaries.
  - The balance of N_2 fixation and denitrification in the Bay is highly variable, but there appears to be a net loss of N in the overall system.
  - Sediment regeneration of ammonium under dark conditions is low relative to benthic dissolved oxygen demand.
  - Sediment regeneration of ammonium decreases with increases in sediment chlorophyll *a* concentration, indicating that the microphytobenthos is important in regulating water column N concentrations.
  - There is very little, if any, P flux out of the sediments with the exception of the Western Bay/Shelf area.
  - High rates of organic C and N fluxes occur, both into and out of sediments over diel cycles (particularly in the central and western Bay).
  - Phosphorus sorption-desorption varies strongly as a function of temperature and salinity.
  - The decreasing bayward gradient in iron content of sediments has implications in P availability, sulfide toxicity, and primary production in the benthos.

Table 5.1: Research topics defined by Question 2 (cells in the matrix) and key references to the associated research.

	Spatial Variation	**Temporal Variation**
Water Quality Patterns and Trends	Fourqurean et al. 1993; Boyer et al. 1997; Burd & Jackson 2002	Boyer et al. 1999; Burd & Jackson 2002
Overall Nutrient Budget	Rudnick et al. 1999; Cerco et al. 2000	Rudnick et al. 1999; Cerco et al. 2000
External Nutrient Loading		
• Terrestrial Inputs		
• Everglades	Walker 1998; Rudnick et al. 1999	Walker 1998; Rudnick et al. 1999
• Mangroves	Childers et al. 1999; Davis et al 2001; Sutula et al. 2001, (in press)	Childers et al. 1999; Davis et al. 2001; Cable et al. 2001, Sutula et al. 2001, (in press
• Keys	Kruczynski 1999	
• Atmospheric Inputs	Nuttle et al. 2000	
• Groundwater Inputs	Shinn et al. 1994; Corbett et al. 1999, 2000; Price & Swart 2002	
• Gulf of Mexico	Rudnick et al. 1999	
• Atlantic Ocean	Szmant & Forrester 1996	
Exports of Nutrients to Reef Tract	Lapointe & Clark 1992; Swart 2001	
Internal Nutrient Cycling		
• N2 Fixation	Cornwell 2001	
• Benthic Flux	Rudnick 1999; Carlson and Yarbro 1999; Yarbro and Carlson 1999; Chambers et al. 2001; Yarbro and Carlson (in review)	
• Nitrification/Denitrification	Kemp & Cornwell 2001	Kemp & Cornwell 2001
• Microbial Loop	Cotner et al. 2000; Boyer & Dailey (in prep)	Boyer & Dailey (in prep)
• DOM Remineralization	Boyer & Dailey (in prep)	Boyer & Dailey (in prep)
Seagrass Effects on Water Quality		
Higher Trophic Level Effects on WQ		
Water Quality Modeling	Cerco 2000	

Patterns and Trends in Water Quality

A network of water quality monitoring stations was established in 1989 (and funded by SFWMD in 1991) to explicate both spatial patterns and temporal trends in water quality in an effort to elucidate mechanisms behind the recent ecological change. One of the primary purposes for conducting long-term monitoring projects is to be able to detect trends in the measured variables over time. These programs are usually initiated as a response to public perception (and possibly some scientific data) that 'the river-bay-prairie-forest-etc. is dying'. In the case of Florida Bay during 1987, the impetus was the combination of a seagrass die-off, increased phytoplankton abundance, sponge mortality, and a perceived decline in fisheries.

Period of Record

Climactic changes occurring over the data collection period of record had major effects on the health of the bay. Precipitation rebounded from the drought during the late 80's being greater than the long-term average (9.2 cm mo^{-1}) for 9 of the last 12 years (Fig 5.2.). Early in the record, salinity and total phosphorus (TP) concentrations declined baywide while turbidity (cloudiness of the water) increased dramatically. The salinity decline in Eastern and Central Florida Bay was dramatic early on and has since stabilized into a regular seasonal cycle (Fig. 5.3). The box-and-whisker plots presented in this and following figures show the range (boxes are quartiles; whiskers include 90% of data) and median (line in box) of the monthly data. Some of this decrease in Eastern Bay could be accounted for by increased freshwater flows from the Everglades but declines in other areas point to the climactic effect of increased rainfall during this period. The Central Bay continues to experience hypersaline conditions (>35) during the summer but the extent and duration of the events is much smaller.

Chlorophyll *a* concentrations (CHLA), a proxy for phytoplankton biomass, were particularly dynamic and spatially heterogeneous (Fig. 5.4). The Eastern Bay generally has the lowest CHLA while the Central Bay is highest. In the Eastern Bay, which makes up roughly half of the surface area of Florida Bay, CHLA has declined by 0.9 µg l^{-1} or 63%. Most of this decline occurred over a few months in the spring/summer of 1994 and has remained relatively stable. The isolated Central Bay zone underwent a 5-fold increase in CHLA from 1989-94, and then rapidly declined to previous levels by 1996. In Western Florida Bay, there was a significant increase in CHLA, yet median concentrations remained modest (2 µg l^{-1}) by most estuarine standards. There were significant blooms in Central and Western Bay immediately following Hurricanes Georges (Nov. 1998) but it was Hurricane Irene's large rainfall input (Oct. 1999) which spiked a large bloom all throughout the bay. It is important to note that these changes in CHLA (and turbidity) happened <u>years</u> after the poorly understood seagrass die-off in 1987. It is possible that the death and decomposition of large amounts of seagrass biomass might partially explain some of the changes in water quality of Florida Bay but the connections are temporally disjoint and the processes indirect and not well understood.

As mentioned previously, TP concentrations have declined baywide over the 12-year period of record (Fig. 5.5). As with salinity, most of these declines occurred in the early record. Unlike most other estuaries, increased terrestrial runoff may have been partially responsible for the decrease in TP concentrations in the Eastern Bay. This is because the TP concentrations of the runoff are at or below ambient levels in the bay. The elevated TP in the Central Bay is mostly due to concentration effect of high evaporation. It is important to understand that almost all the phosphorus measured as TP is in the form of organic matter which is less accessible to plants and algae than inorganic phosphate.

The dissolved inorganic nitrogen pool (DIN) is made up of three components: ammonium (NH_4^+), nitrate (NO_3^-), and nitrate (NO_2^-). The Western Bay is lowest in DIN; phytoplankton in this region may be limited by N availability on a regular basis (Fig. 5.6). DIN in the Eastern Bay is a little higher and is mostly in the form of NO_3^- while highest levels are found in the Central Bay as NH_4^+.

Turbidity in the Central and Western Bays have increased tremendously since 1991 (Fig. 5.7). Turbidity in Eastern Bay increased 2-fold from 1991-93, while Central and Western Bays increased by factors of 20 and 4, respectively. Generally, the Eastern Bay has the clearest water that is due to a combination of factors such as high seagrass cover, more protected basins, low tidal energy, and shallow sediment coverage. We are unsure as to the cause but the loss of seagrass coverage may have destabilized the bottom so that it is more easily disturbed by wind events.

An extensive set of contour maps of water quality parameters in Florida Bay is available at http://serc.fiu.edu/wqmnetwork/.

Recent Conditions

Most water quality variables during 2001 generally followed typical annual trends but there were a couple exceptions. Unlike some years, all regions of the bay experienced a prolonged period of hypersalinity during the summer months. Most of this was due to the dry year prior that set up the system for this occurrence. The annual pattern in CHLA was unremarkable; no blooms reported. TP values declined from the very high fall 2000 levels and have returned to normal. Western Bay showed elevated DIN during the early part of the year but was not unreasonable compared to other years. Turbidity continues fluctuate at post 1993 levels. Note that the high turbidities observed in the Western Bay during the winter also correlated with elevated TP.

NOAA AOML also has a water quality monitoring program in Florida Bay. Its primary purpose is to measure physical aspects of the system (see Question 1) but there also is a nutrient component to the sampling. An example is the analysis of SRP (Fig. 5.8) using long-path-length liquid waveguide technology from Zhang and Chi (2002).

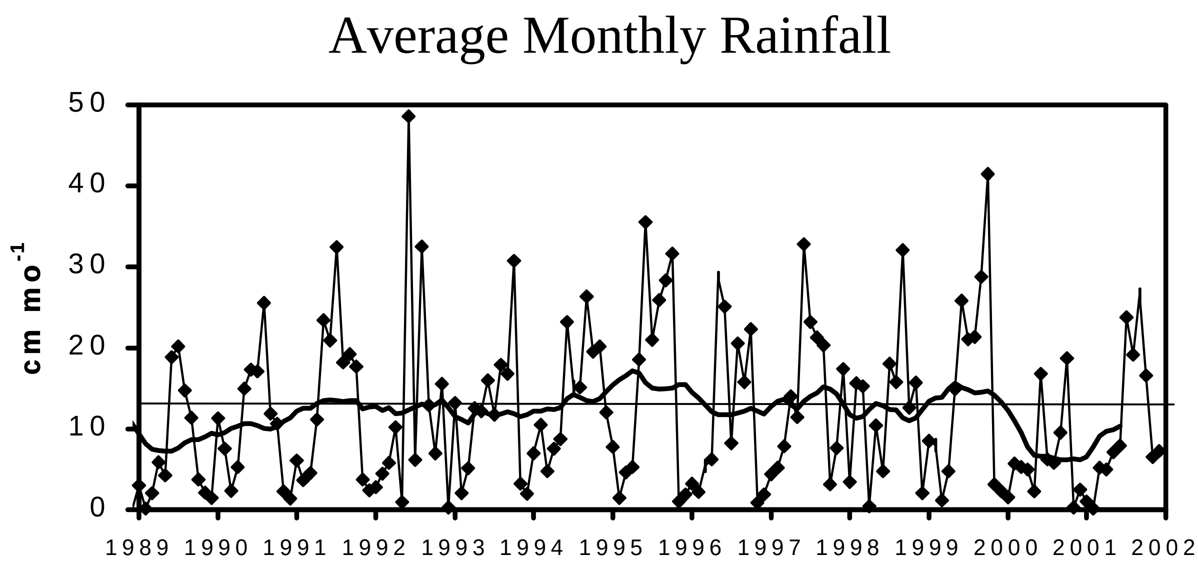

Figure 5.2: Monthly average rainfall in the Florida Bay area.

Median Salinity

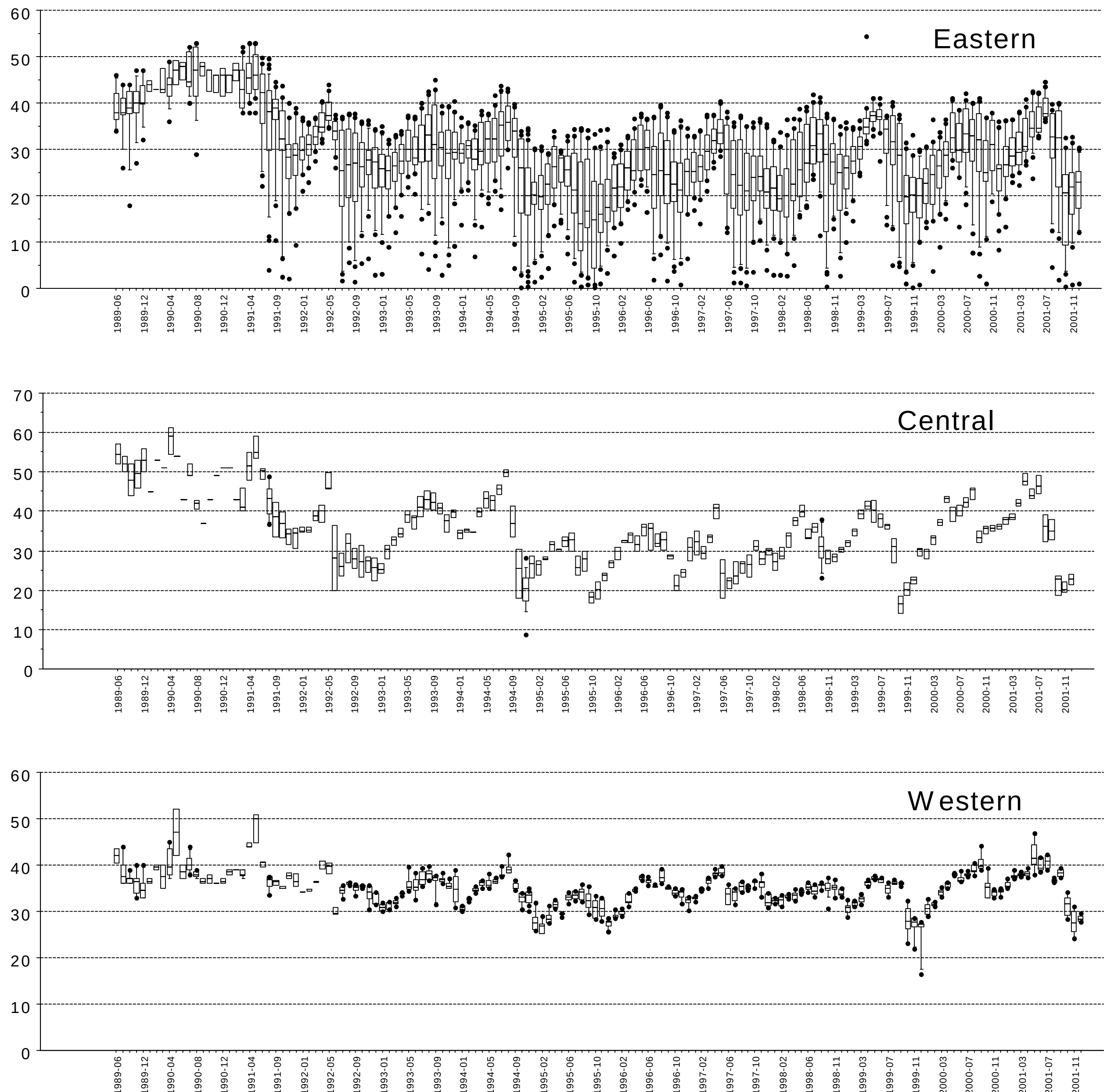

Figure 5.3: Monthly median salinity in the three Florida Bay zones.

Median Chlorophyll a

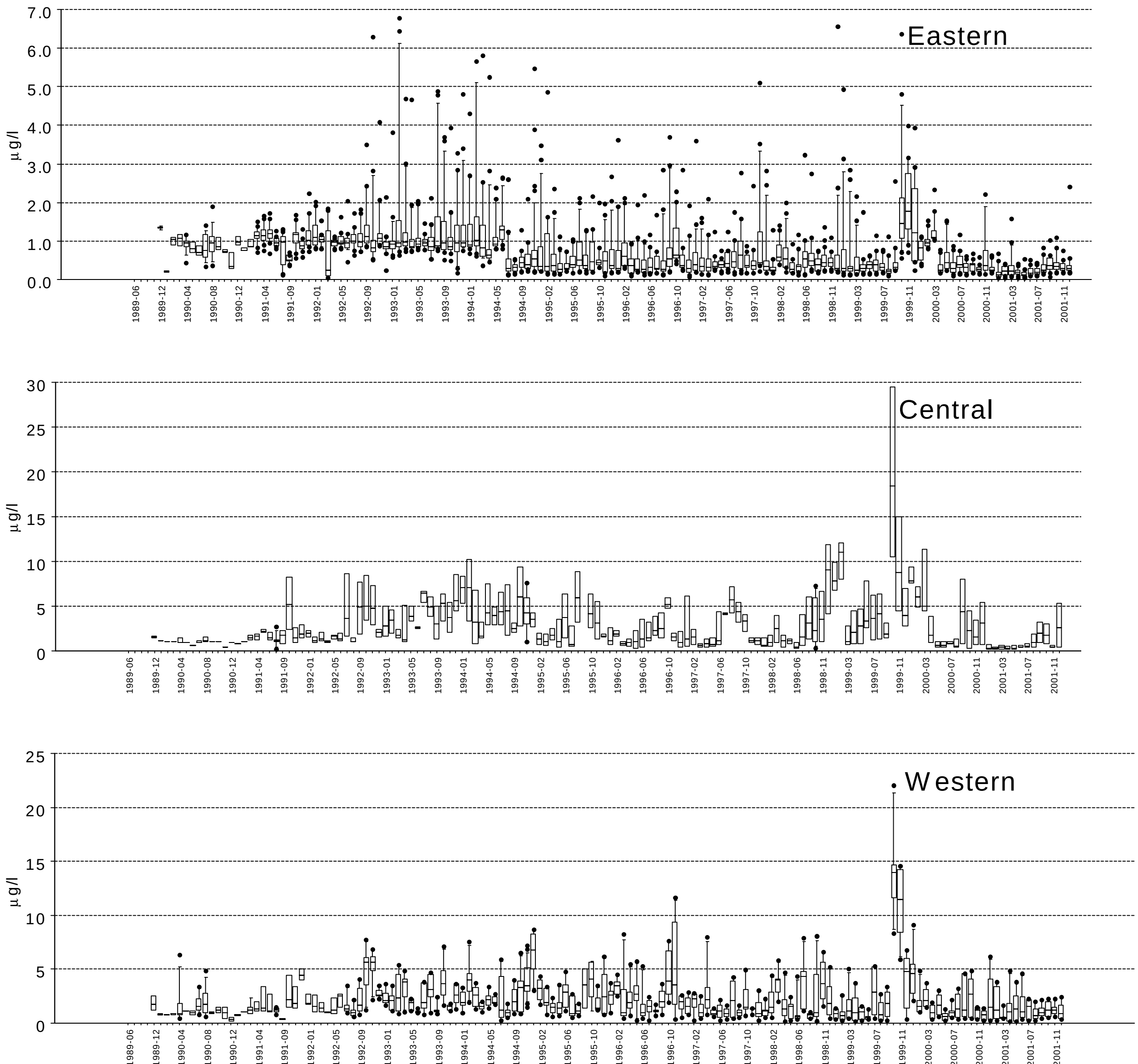

Figure 5.4: Monthly median CHLA in the three Florida Bay zones.

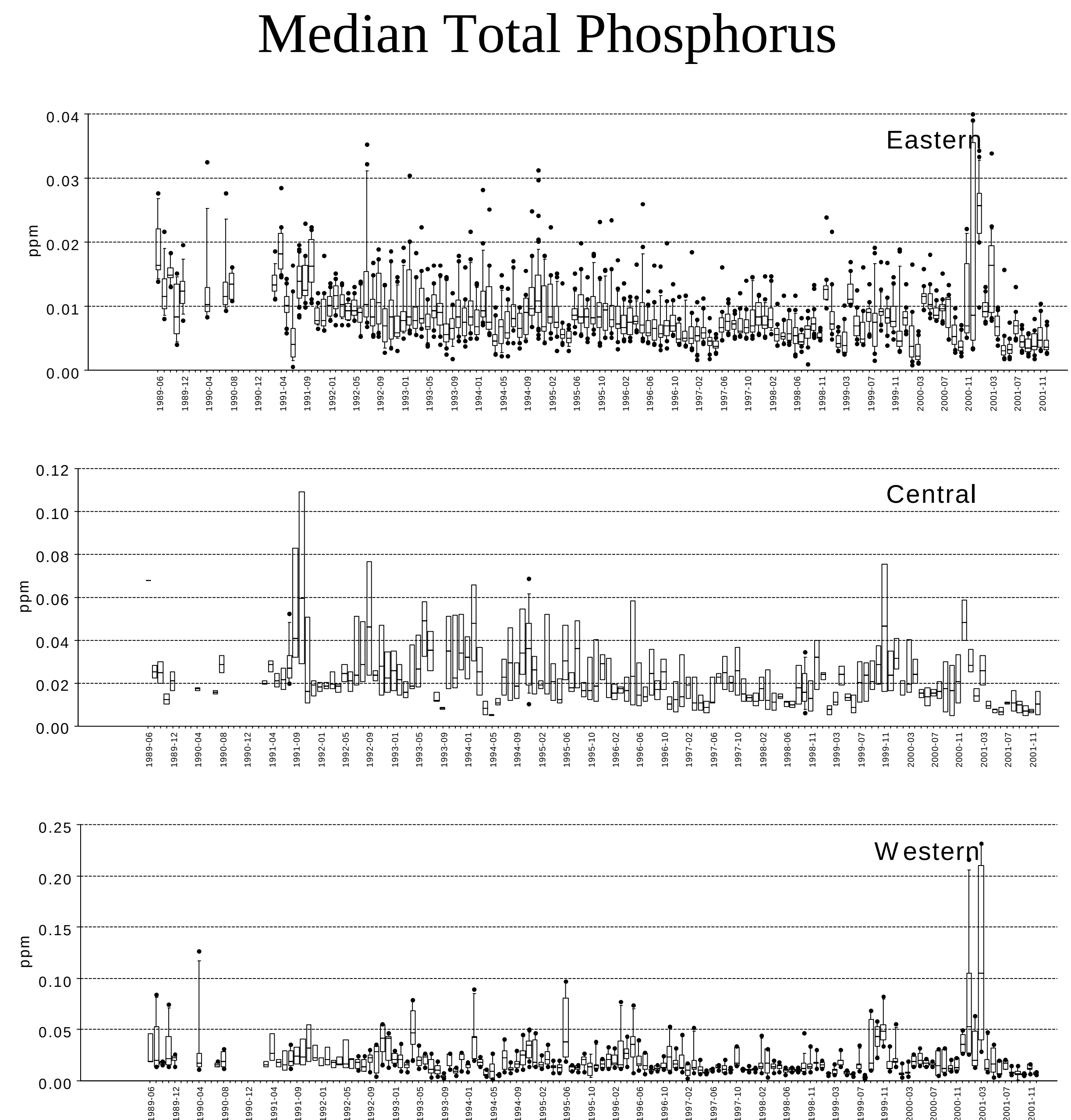

Figure 5.5: Monthly median TP in the three Florida Bay zones.

Median Dissolved Inorganic Nitrogen

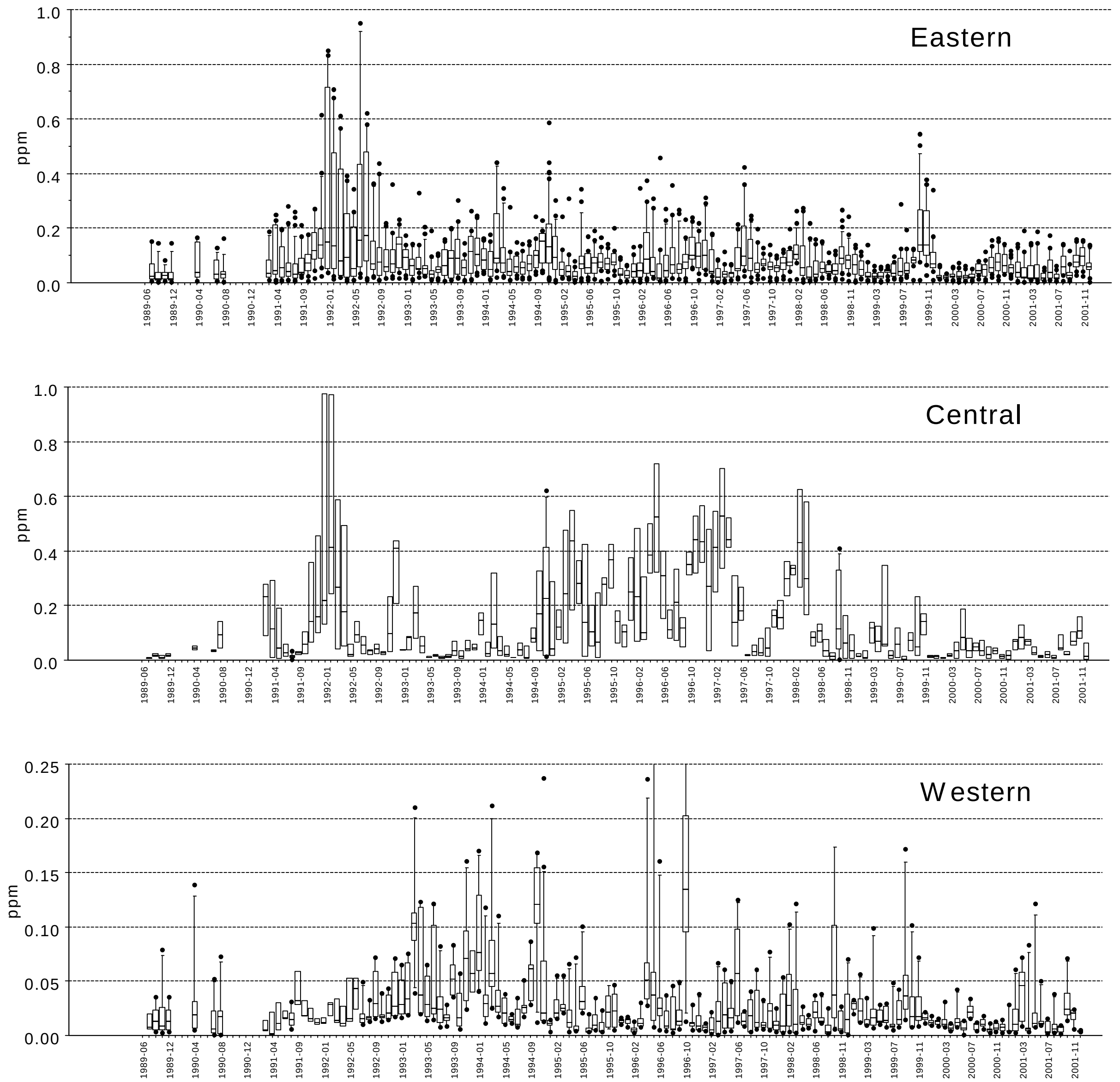

Figure 5.6: Monthly median DIN in the three Florida Bay zones.

Median Turbidity

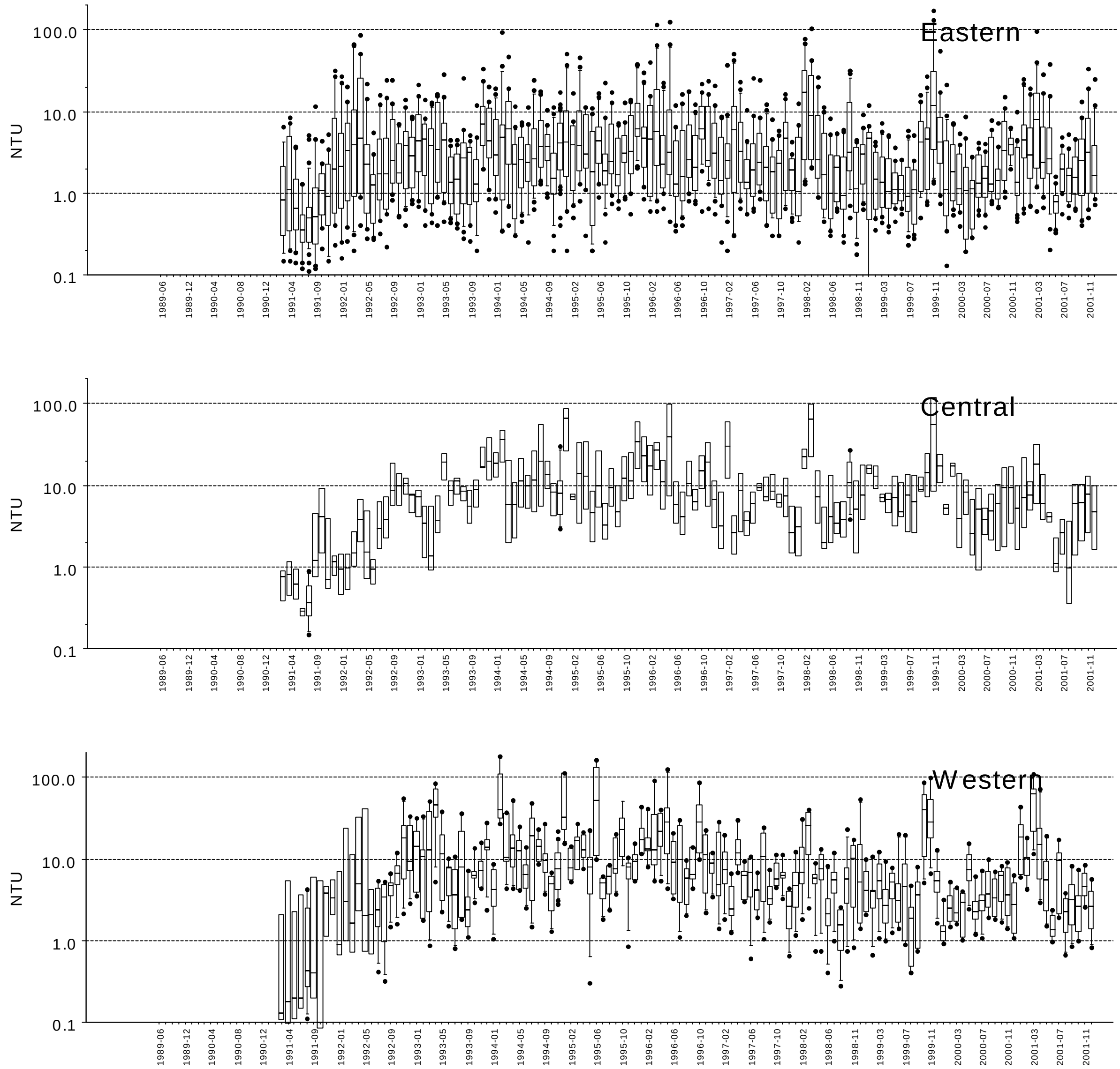

Figure 5.7: Monthly median turbidity in the three Florida Bay zones.

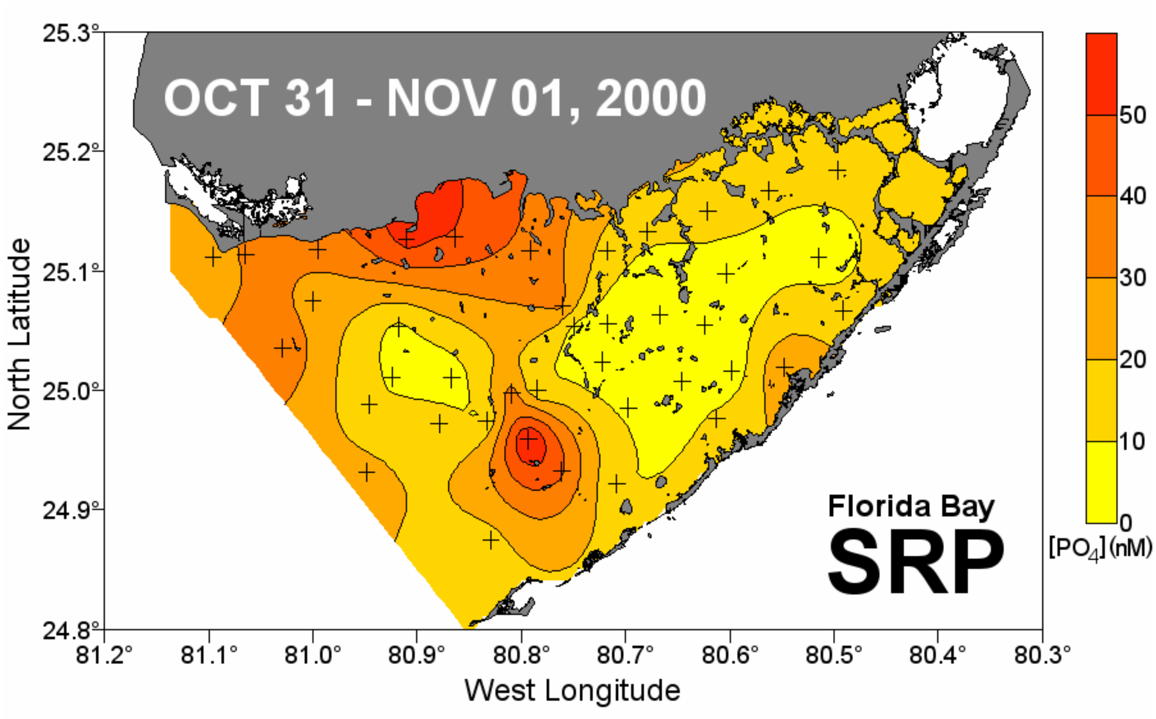

Figure 5.8: Water column phosphate concentration in Florida Bay.

Exogenous Sources of Nutrients

A budget of Florida Bay's exogenous nutrient sources that was estimated for the 2001 Florida Bay Conference included inputs from the Everglades, Keys wastewater and stormwater, saline groundwater, the Gulf of Mexico, the Atlantic Ocean, and the atmosphere. Results from this exercise, with revision of the estimated saline groundwater source, are presented in Figures 5.9-5.11.

Nutrient inputs from the Everglades: Taylor Slough/C-111 and Shark River

Nutrient outputs from the Everglades in this budget have been estimated from inputs to Everglades National Park wetlands from canals as in Rudnick et al. (1999). This approach can only be considered a rough estimate because of nutrient processing during transport through the southern Everglades. However, these estimates have less uncertainty than most other components of the Bay's nutrient budget. The accuracy of estimates for southeast Everglades nutrient outputs is indicated by results of Sutula et al. (in press). This study found that TN and TP fluxes from the mouths of mangrove creeks into Florida Bay in 1997 were similar to estimates to estimated inputs to the wetland that year (TN loads differed by 7% and TP loads differed by one metric ton per year).

Studies of nutrient export from Taylor River, Trout Creek, and McCormick Creek (Sutula et al. in press, Davis et al. in press) have provided insights of the relationship between patterns of freshwater discharge and nutrient dynamics and output to Florida Bay. Nutrient outputs have been found to increase with increasing water discharge. As observed for inflows to Everglades National Park wetlands from canals, this increase is not linear; flow weighted mean nutrient concentrations decrease with increasing discharge (Rudnick et al. 1999; Figure 5.12). Output of phosphorus to Florida Bay is mostly as dissolved organic P, but is very low in magnitude. During the dry season, both suspended solids and P are imported northeast Florida Bay mangrove ecotone from the Bay. Output of nitrogen is also largely as dissolved organic N, but this quantity is high, resulting in a very high TN: TP in creek outputs (molar ratio average near 200).

During the next year, RECOVER (the monitoring and assessment program of the Comprehensive Everglades Restoration Plan) will expand the network of creek discharge and nutrient sampling stations to include new sites along the Florida Bay coastline and western Everglades' rivers. A total of eight paired (upstream-downstream) stations are planned, including four creeks entering Florida Bay and four rivers entering the Gulf of Mexico. It should also be noted that the Florida Coastal Everglades LTER is providing information on nutrient processing in the southern Everglades and mangrove zone, with particular emphasis on the formation, transport, and decomposition of dissolved organic matter.

Ground water

The input of nutrients to Florida Bay via ground water remains highly uncertain. No new estimates of ground water flux have made since the 2001 conference. At that time, it was evident that subsurface fresh water inputs are negligible. Ground water beneath Florida Bay and its mangrove ecotone along the Everglades coast are saline (Price 2001, C. Reich and G. Shinn [pers. comm.]). Thus, fresh ground water beneath the Everglades that flows toward Florida Bay appears to rise toward the surface, over denser saline water, to the north of the Bay boundary (Price 2001).

In contrast to fresh ground water, significant advection of saline ground water into the Bay may occur from beneath it. Based on groundwater tracer (radon, methane) concentrations, Corbett et al. (1999, 2000) have estimated a Bay-wide vertical groundwater flux of about 1 cm/d. The nutrient budget presented at the 2001 Florida Bay Conference assumed this value and nutrient concentrations of 0.1 µM TP, 1 µM DIN, and 10 µM TN. These concentrations are typical of wells at pristine sites in the Florida Keys (G. Shinn [pers. comm.]). However, C. Reich and Shinn (pers. comm.) now report that these concentrations are considerably lower than in wells throughout Florida Bay. Over a four-year period, concentrations averaged about 1.5 µM TP, 80 µM TN, and 44 µM NH_4. Still assuming 1 cm/d groundwater flux, these higher concentrations would result in a groundwater nutrient flux of 38 MT/y for TP, 8,800 MT/y for TN, and 5,000 MT/y for DIN. Compared to nutrient fluxes from the Everglades, these estimated groundwater fluxes are about 10 times higher for TP, about 6 times higher for TN, and more than 100 times higher for DIN.

If this groundwater flux estimate of DIN were accurate, it would represent about 75% of all inorganic N inputs to the Bay. Furthermore, at such a high concentration this inorganic N would be readily available for algal and SAV productivity (in contrast to low-concentration flux from the Gulf of Mexico). It should be noted that this estimated groundwater DIN flux is equivalent to 18 µmoles m^{-2} h^{-1} or roughly half of the median nocturnal nutrient flux across the sediment-water interface, as measured along the northern Florida Bay coast. It is also roughly equal to the median nocturnal benthic flux found in the interior bay (P. Carlson [pers. comm.]). The surprisingly high magnitude of the groundwater DIN flux estimate, combined with the fact that groundwater is usually hypersaline, is grounds for skepticism regarding the estimated 1 cm/d groundwater flux as a rate that occurs commonly through the Bay. This does not preclude the possibility that large inputs of ground water occur at some locations in the Bay.

Atmospheric, Keys wastewater and stormwater nutrient inputs, and the Gulf of Mexico

The remaining components of the Florida Bay nutrient budget (atmospheric, Keys wastewater and stormwater, and the Gulf of Mexico) have not been revised since the 2001 conference. Atmospheric deposition is certainly an important nutrient source, particularly with regard to the relatively high input of inorganic nitrogen. The estimates in Figures 5.9 to 5.11 are derived from a study by T. Meyers in 1999 and 2000 on Long Key (T. Meyers [pers. comm.]). While bulk deposition of nitrogen can be estimated from a long-term NADP site in Everglades National Park, little data is available to estimate dry deposition of N or P. Furthermore, P estimates in south Florida are often suspect because of the contamination of low ambient concentrations (Redfield 2002). Estimates of the Florida Keys and Gulf of Mexico contributions are based on methods and data described in Rudnick et al. (1999). The Keys estimate entails far less uncertainty than the Gulf estimate. It should be noted that the Gulf contribution provided here (Figures 5.9 – 5.11) probably overestimate inputs to interior Florida Bay, because the flow meters that produced data used in the calculation were west of Florida Bay's mud banks. A large proportion of water flux measured by these flow meters never entered the bay. It should also be noted that a large discrepancy between the estimate of Rudnick et al. (1999) and Cerco et al. (2000) exists. The latter is based on flow fields derived from a hydrodynamic model (Table 5.3).

Table 5.3: Comparing nutrient budgets for Florida Bay

(From Cerco et al. 2000)

Florida Bay Nutrient Budgets (positive into system)

	Rudnick et al.		Model Dry Season		Model Wet Season	
	Total Phosphorus (kg d^{-1})	Total Nitrogen (kg d^{-1})	Total Phosphorus (kg d^{-1})	Total Nitrogen (kg d^{-1})	Total Phosphorus (kg d^{-1})	Total Nitrogen (kg d^{-1})
Everglades	7.1	685	3.0	679	9.1	1753
Atmosphere	104.1	1945	127.0	2393	127.0	2393
Keys loads	115.1	466	54.9	238	54.9	238
Western boundary	1112.3	21918	192.7	3105	-589.6	-6217
Keys passes	-493.2	-32877	101.8	2068	158.4	4154
Net	845.5	-7863	479.4	8483	-240.2	2321

Summary

The major source of TP and TN was the Gulf of Mexico (Fig. 5.9 and 5.10) and the major source of DIN was ground water (Fig. 5.11). The smallest source of TP was Taylor Slough/C-111 (Fig. 9). The minimal input of TN was from the Keys (Fig. 5.10), while minimal inputs of DIN were from Shark River and Taylor Sough/C-111 (Fig. 5.11).

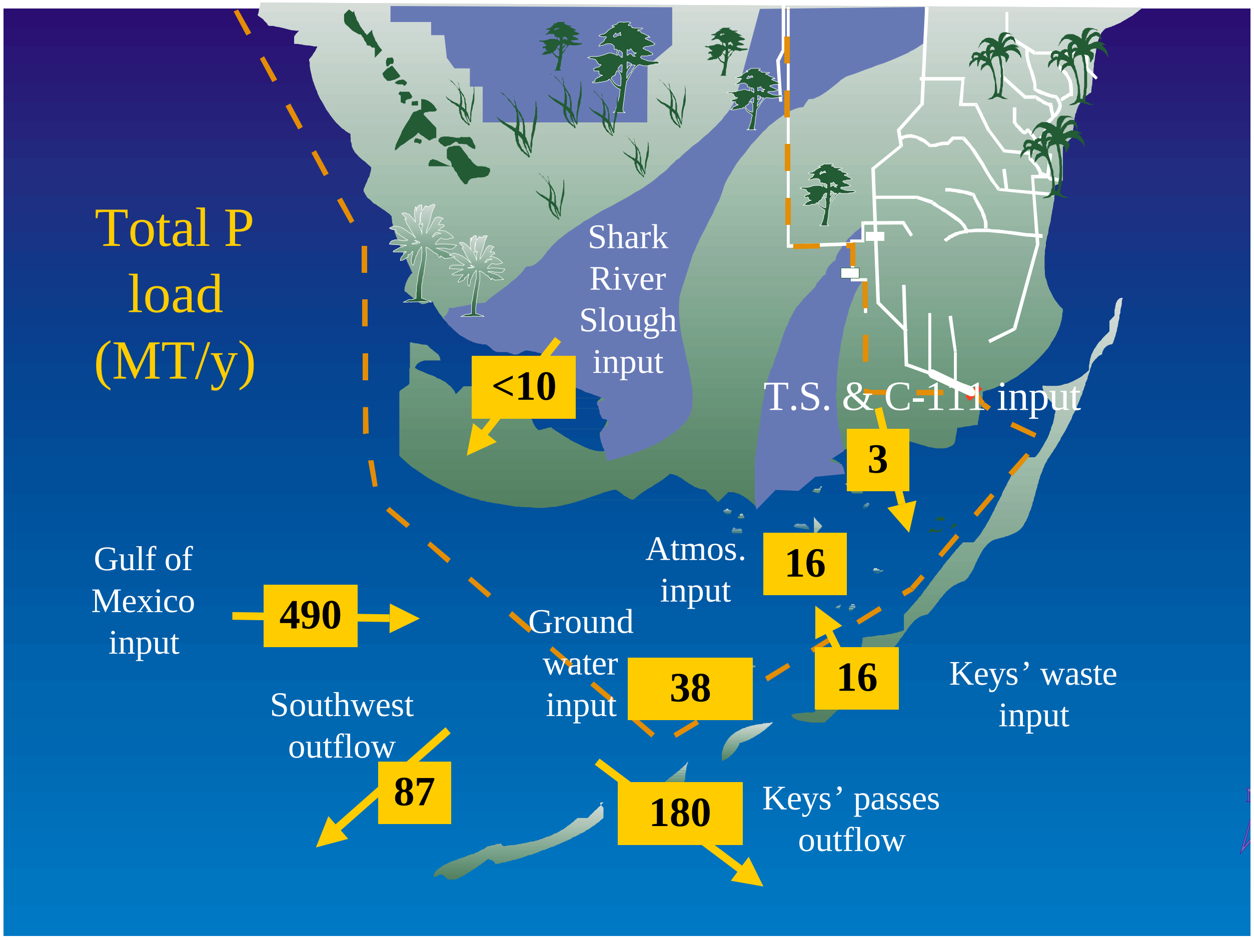

Figure 5.9. Estimates of the annual exchange of total phosphorus at Florida Bay's boundaries. Everglades estimates are annual median inputs to wetlands from canals (since 1979 for Shark Slough, and 1984 for Taylor Slough and C-111 basin).

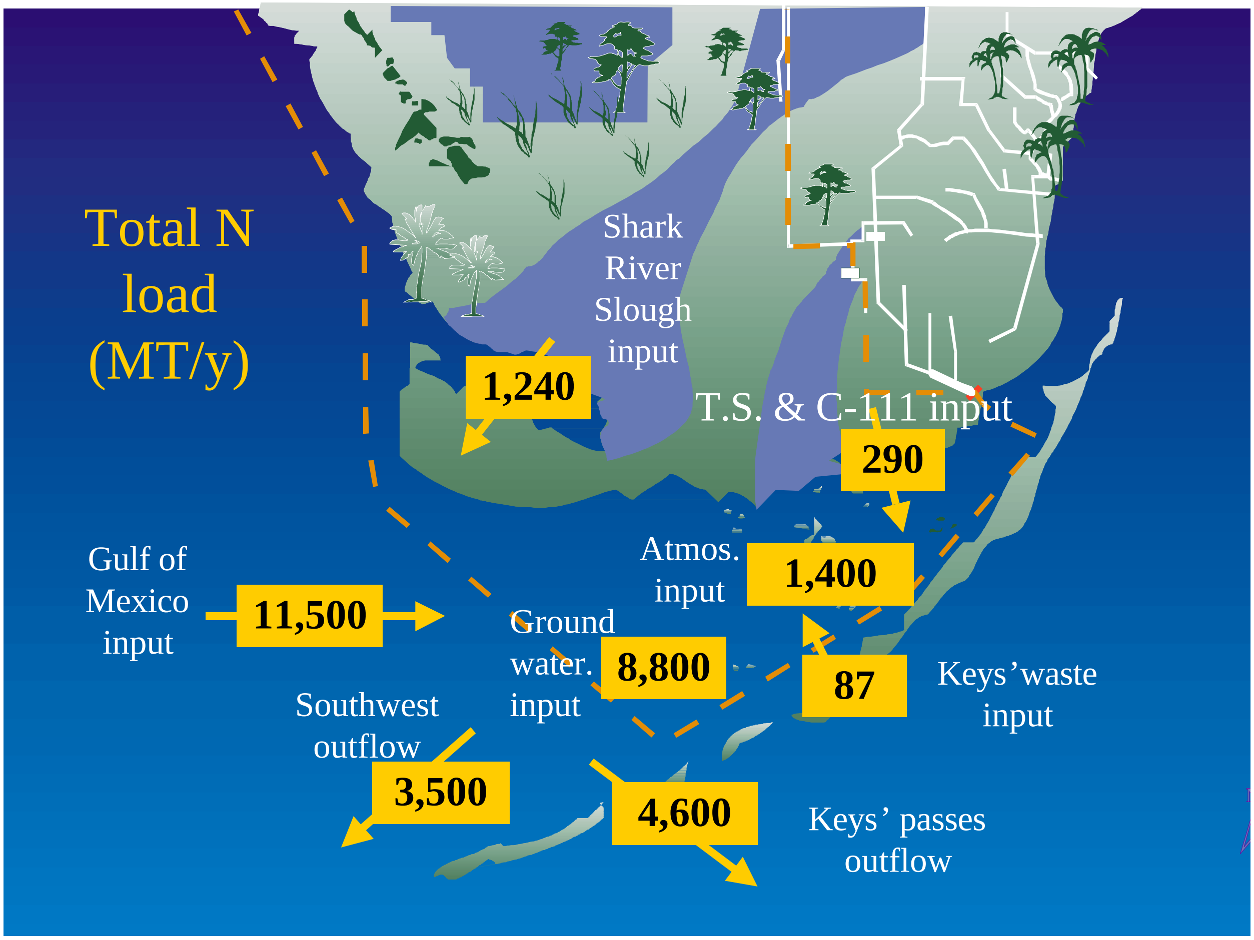

Figure 5.10. Estimates of the annual exchange of Total N at Florida Bay's boundaries. Everglades estimates are annual median inputs to wetlands from canals (since 1979 for Shark Slough, and 1984 for Taylor Slough and C-111 basin). Note that flow weighted mean TN concentrations have been consistently decreasing since 1985 in both systems and medians provided here may be higher than during recent years.

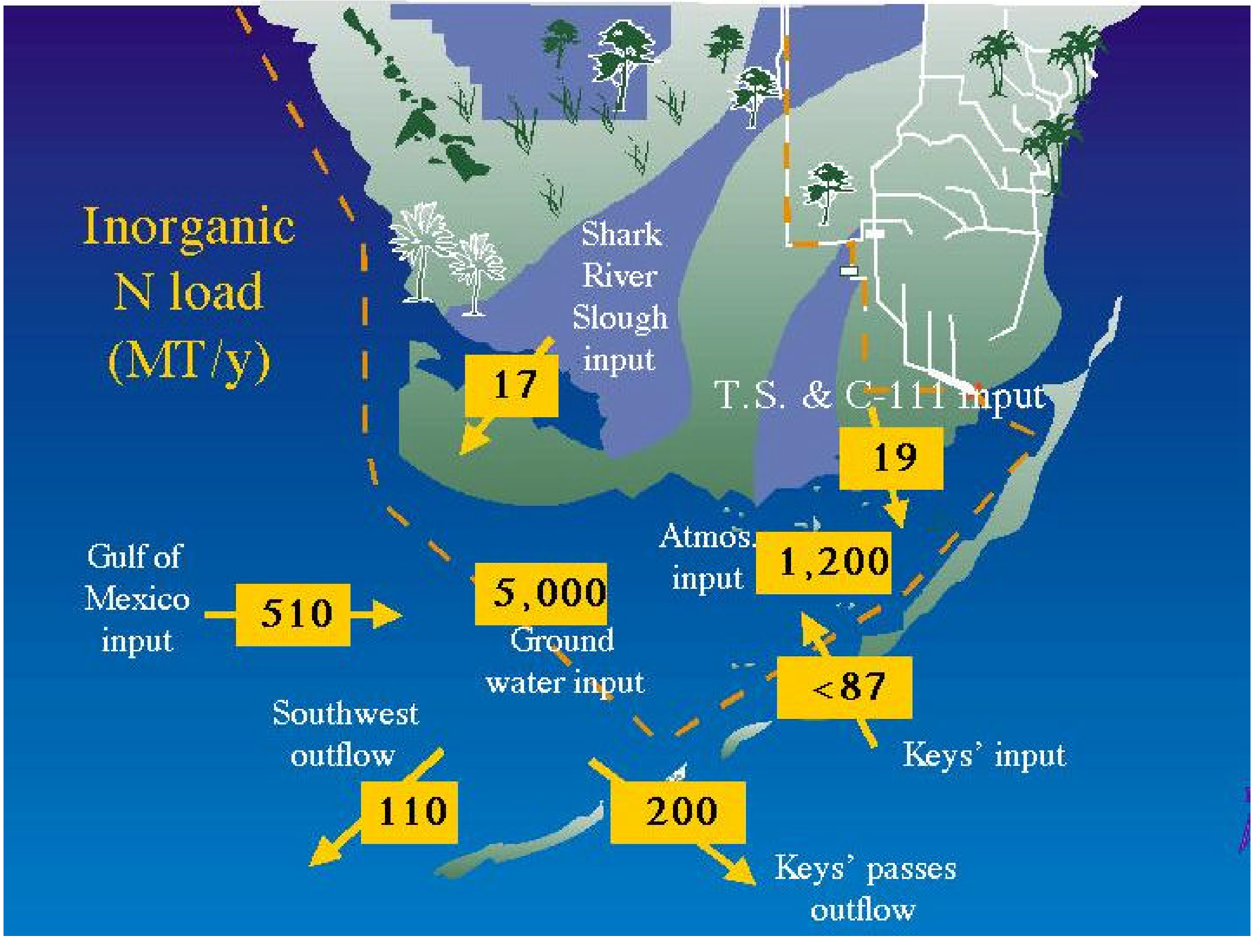

Figure 5.11. Estimates of the annual exchange of Inorganic N at Florida Bay's boundaries. Everglades estimates are annual median inputs to wetlands from canals (since 1979 for Shark Slough, and 1984 for Taylor Slough and C-111 basin).

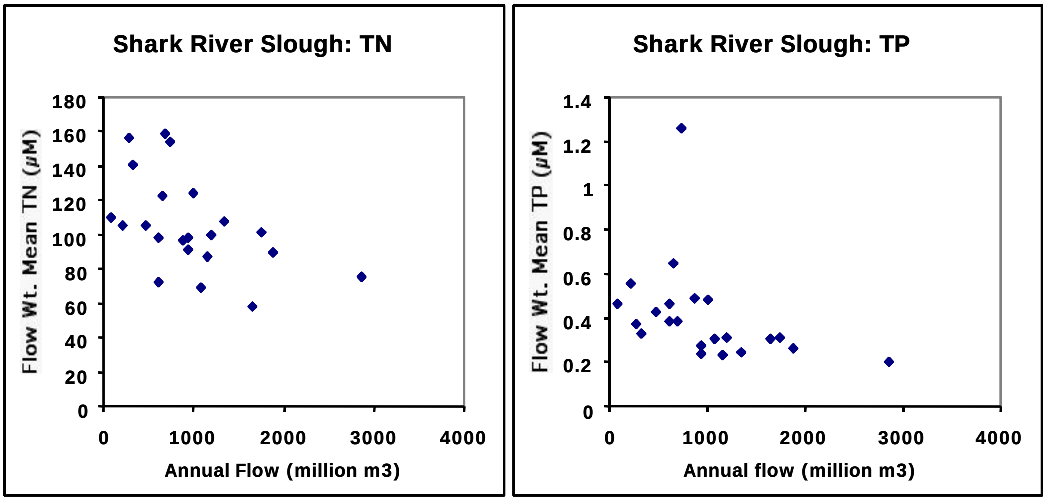

Figure 5.12. Relationship between TN and TP concentrations (annual flow weighted mean) in waters flowing into Shark River Slough and annual water discharge into the Slough.

Internal Nutrient Cycling

Benthic nutrient fluxes

In situ benthic metabolism and nutrient regeneration were measured seasonally for 3 years (through 2000) at five sites near the northern Florida Bay coast (Rudnick et al. 2001) and for 1.5 years (1997-1998) at six bay sites away from the northern coast (Carlson 1999). Additional flux measurements have been made more recently in sediment cores (Cornwell et al. 2003). The most notable results of these studies have been that phosphorus fluxes are very low (typically not significantly different from zero) and that inorganic N fluxes from sediment to water are surprisingly low. Sediments consistently removed nitrate plus nitrite from the water column under dark and light conditions. Relative to rates of sedimentary oxygen uptake in the dark, ammonium release has been found to be very low. Median O:N molar ratios in dark chambers at northern coastal sites greatly exceeded that expected from the mineralization of algal or seagrass detritus, ranging from 51 to 124 (O uptake:N release) (Rudnick et al. 2001). Given the high organic matter concentrations of central Florida Bay, the finding of consistently low (less than 50 $\mu mol\ m^{-2}\ h^{-1}$) ammonium fluxes from Rankin Lake sediments (by Carlson 1999; Kemp and Cornwell 2001) is surprising.

Studies by Cornwell et al. (2000) and Kemp and Cornwell (2001) provide insights of mechanisms that explain the observed low rates of ammonium regeneration. They found that ammonium fluxes were negatively correlated with benthic chlorophyll *a* concentrations (Fig. 5.13). This may be caused by benthic algal stimulation of coupled nitrification-denitrification. These studies found that net N_2 fluxes were typically from sediment to water (dentrification exceeding nitrogen fixation). Denitrification rates (dark N_2 fluxes) at six sites averaged 127 ± 87 roughly 100 $\mu mol\ m^{-2}\ h^{-1}$ in August and 65 ± 82 $\mu mol\ m^{-2}\ h^{-1}$ in March. These fluxes greatly exceeded ammonium fluxes. Further support for the inference that low inorganic N regeneration is attributable to coupled nitrification-denitrification was provided by in situ hypoxia experiments (Rudnick et al.2001). Dissolved oxygen and nutrients were followed in time series over 28 hours in dark benthic chambers. When dissolved oxygen in the water column dropped below 0.2 mg/L, ammonium fluxes increased five fold.

Yarbro and Carlson (in review) measured benthic fluxes of filterable reactive phosphorus (FRP), NH_4^+, silicate, TP, TN, dissolved organic phosphorus (DOP), and DON in seagrass beds in the Eastern Bay (Sunset Cove and Swash Keys), Central Bay (Rankin Lake and Calusa Key), and Western Bay (Johnson and Rabbit Key Basins). FRP fluxes ranged from uptake of 3 $\mu mol\ m^{-2}\ h^{-1}$ in Johnson Key Basin in the western Bay to releases of 1-2 $\mu mol\ m^{-2}\ h^{-1}$ in the eastern Bay. Dissolved organic phosphorus (DOP) fluxes (2-4 $\mu mol\ m^{-2}\ h^{-1}$) were considerably higher than FRP fluxes and were more often released from the benthos, especially at central and western Bay sites. These small fluxes are in sharp contrast to the large phosphorus pool in surficial sediments (1-12 $\mu mol\ gDW^{-1}$).

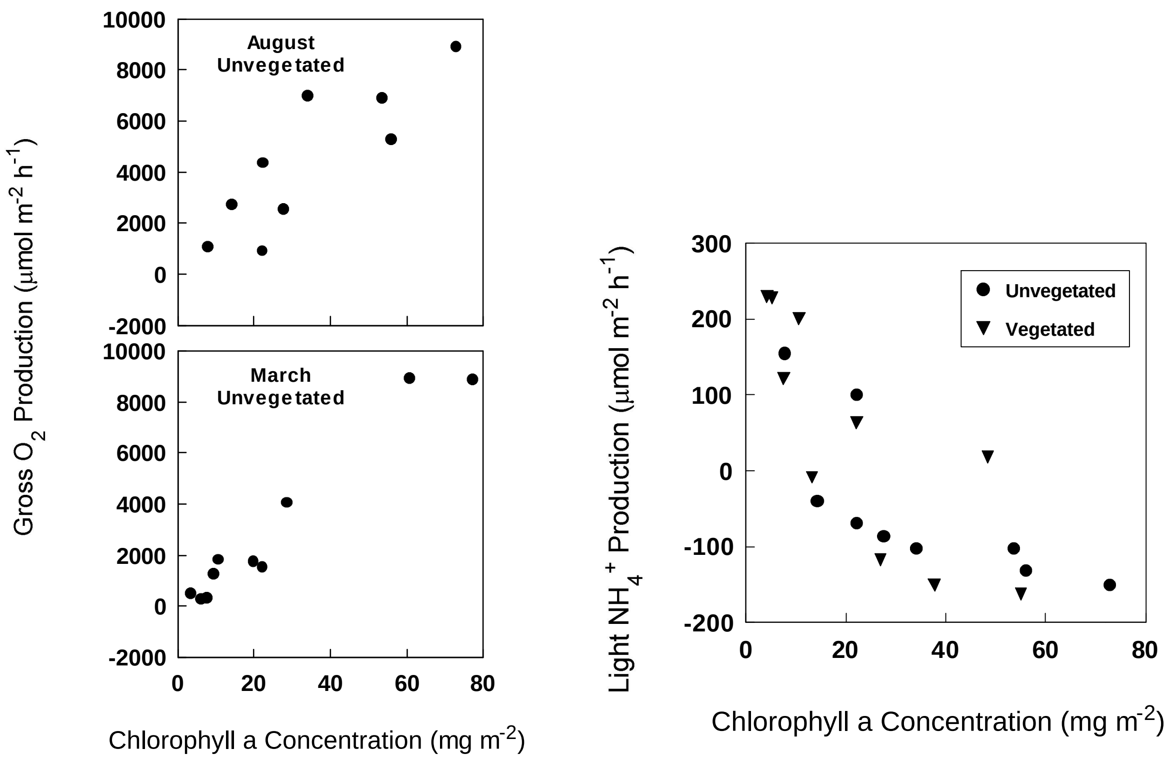

Figure 5.13. Measured rates of denitrification (dark N_2 flux) were much higher than would be predicted from estimated N loading rates to Florida Bay. Overall, rates averaged 127 ± 87 µmol m^{-2} h^{-1} in August and 65 ± 82 µmol m^{-2} h^{-1} in March for all Bay sites.

Additionally, the sharp increase in sediment phosphorus from east to west in the Bay was not reflected in benthic fluxes. Keeping in mind that these fluxes represent net flux to or from the seagrass community, we estimate that ammonium and the sum of FRP and DOP fluxes can meet 20-50% of the phytoplankton demand in the eastern and western regions of Florida Bay, but only 5-10% of the phytoplankton demand in the highly productive, *Synechococcus*-dominated north central Bay.

Internal nutrient cycling: carbonate-P-Fe relations

A study by Chambers et al. (2001) documented the spatial variation in sediment phosphorus, iron and sulfur. Total sediment phosphorus decreases on a west-east gradient across Florida Bay, similar to patterns of surface water quality. Mineral sulfides and extractable iron in Florida Bay sediments decrease on a north-south gradient. Most inorganic phosphorus in the sediment is associated with abundant calcium carbonate minerals and not with reactive iron oxides that occur in very low concentrations. Iron availability limits sulfide mineral formation, and dissolved sulfide concentrations in Florida Bay sediments are high. Experimental addition of reactive iron to seagrass plots in Florida Bay stimulated phosphorus retention in the sediment and buffered plants from toxic sulfide accumulation. Phosphorus availability to seagrass still appears to limit production in carbonate sediments more than sulfide toxicity. Generation of inorganic phosphorus in seagrass sediments may occur directly via mineralization of organic matter, and indirectly via concomitant carbonate mineral dissolution (Ku et al. 1999).

Role of sediment resuspension in P cycling

Phosphorus is retained on the surface of calcium carbonate sediments (Zhang and Fischer 2001). When sediments are resuspended, phosphate that is weakly bound to particle surfaces is released to the water column within a few minutes where it may be utilized by phytoplankton; coprecipitation of calcium phosphate with calcium carbonate may scavenge dissolved phosphate out of the water column.

Total sedimentary phosphorus (TSP) was fractionated into five chemically defined pools (Zhang and Fischer 2001): 1) adsorbed (readily exchangeable) inorganic and organic P, 2) Fe-bound inorganic P, 3) authogenic apatite calcium carbonate-bound inorganic and organic P, 4) detrital apatite P, and 5) refractory residual organic P. As was noted above (Chambers et al. 2001), this study observed a strong gradient of decreasing TSP from the west (14.6 µmol g^{-1}) to the east (1.2 µmol g^{-1}) across central Florida Bay (Zhang et al. submitted).

Among the five pools, authogenic apatite calcium carbonate-bound P accounted for the largest fraction of P (45% of TSP; Zhang et al. submitted); inorganic P dominated this pool (70-90%). The refractory organic residue (24% of TSP) and Fe-bound inorganic P (19% of TSP) were the second largest pools. Adsorbed P accounted for only 8% of TSP (60% organic P) and detrital apatite P comprised the smallest fraction (5% of TSP). Overall, organic P accounted for 38% of TSP.

Nutrient flux at the sediment-water interface

Yarbro and Carlson (1999) measured silicate fluxes that ranged from -337 µmol m^{-2} h^{-1} at Rankin Lake (Sept. 1997) to 766 µmol m^{-2} h^{-1} at this site (Aug. 1998). Ammonium fluxes ranged from -8.3 µmol m^{-2} h^{-1} at Rankin Lake (Nov. 1998) to 156 µmol m^{-2} h^{-1} at Sunset Cove at this time. Total dissolved nitrogen fluxes were highly variable among sites and sampling dates ranging from -340 µmol m^{-2} h^{-1} at Rabbit Key Basin (Aug. 1998) to 193 µmol m^{-2} h^{-1} at Sunset Cove (Nov. 1998). Dissolved organic nitrogen (DON) also varied among sites and sampling dates, ranging from 5.7 µmol m^{-2} h^{-1} at Swash (May 1998) to 250 µmol m^{-2} h^{-1} at Rabbit Key Basin (Aug. 1998). Net DON flux was always from the sediment to the water column.

Because filterable reactive phosphorus (FRP) concentrations generally were very low, flux estimates were highly variable (Yarbro and Carlson 1999). FRP and total dissolved phosphorus fluxes ranged from net uptakes of -6.23 to -0.02 µmol m^{-2} h^{-1} to sediment release of 0.02 to 11.57 µmol m^{-2} h^{-1}; most fluxes were less than 1 µmol m^{-2} h^{-1}.

Influence of Florida Bay Water Quality on the Reef Tract

Nutrient export through Keys' Passes

The rate of outflow was estimated by Lee and Smith (2000) from measurements in Long Key, Channel 5, and Channel 2 in 1997 and 1998. The long-term mean = 370 m^3/s (11.7 x 10^9 m^3/y). Nutrient concentrations were measured as part of FIU monitoring (Jones and Boyer 2002b), and the flux calculation assumed median concentrations.

The estimated exports (MT/y) were: TP=180; TN=4600; DIN=200 (Fig. 5.9-5.11).

Net fluxes

Based on these estimates, Florida Bay is a sink for approximately half of the inputs of TP and TN and more than 80% of the inputs of DIN. Additional export of N and P from Florida Bay may occur in the form of drift seagrasses and algae, but no quantitative estimates have been made for this flux.

Water Quality Modeling

The water quality model (Cerco et al. 2000; Fig. 5.14 and 5.15) linked modules including water-column eutrophication, seagrass dynamics, sediment diagenesis, solids and nutrient resuspension, and benthic algal production. To our knowledge, this is a first for Florida Bay. In fact, we know of few systems that presently have a model application to rival the current effort in Florida Bay. The model does require substantial upgrading, however, to fully represent processes in the Bay.

Nutrient loads to the bay and surrounding waters from various sources were calculated for the model study. Estimates indicate the atmosphere is the largest of the loading sources to the bay. Runoff from the mainland is the least source of phosphorus and second least source of nitrogen. Paradoxically, runoff appears to be the most intensely studied loading source while large degrees of uncertainty exist in the greatest loads. Attention should be devoted to accurately quantifying atmospheric loads and phosphorus loads from the Keys.

No in-situ measures of nitrogen fixation were available to us. Rates associated with seagrass beds, measured in other systems, were adapted for the model. Estimated nitrogen fixation associated with seagrass leaves equals the estimated atmospheric nitrogen load. The sum of nitrogen fixed in the leaves and roots makes nitrogen fixation the largest single source to the system. To our knowledge, measures of nitrogen fixation are currently being conducted. These measures should be swiftly incorporated into the model and into system nutrient budgets.

Neither were measures of denitrification within benthic sediments available. Rates of denitrification were calculated by the sediment diagenesis model with parameters adapted from Chesapeake Bay. Calculated denitrification roughly equals total nitrogen fixation. Denitrification rates should be measured and used to verify the computations provided by the model.

The model underestimates the amount of nitrogen in both the sediments and water column. Sensitivity analysis indicates the shortfall is unlikely to originate in loading estimates. Either a source of nitrogen has been omitted or the estimated loads are greatly in error. Potential sources of omission or error include groundwater, nitrogen fixation, and denitrification.

The model does not concentrate material in the central basins e.g. hypersalinity. This behavior may be attributed to several factors. First, the underlying hydrodynamic calculations may not concentrate material. Second, the linkage method may introduce errors in the computed hydrodynamic field. Third, the water-quality grid and numerics may introduce artificial dispersion. Dye tracer tests indicate the water quality model qualitatively tracks transport in the hydrodynamic model in Florida Bay. (Transport is not equivalent on the western shelf, due to artificial dispersion and boundary condition specification). The tracer tests lead us to the conclusion that the underlying hydrodynamics prevent computation of hypersalinity and concurrent concentration of nitrogen and other materials.

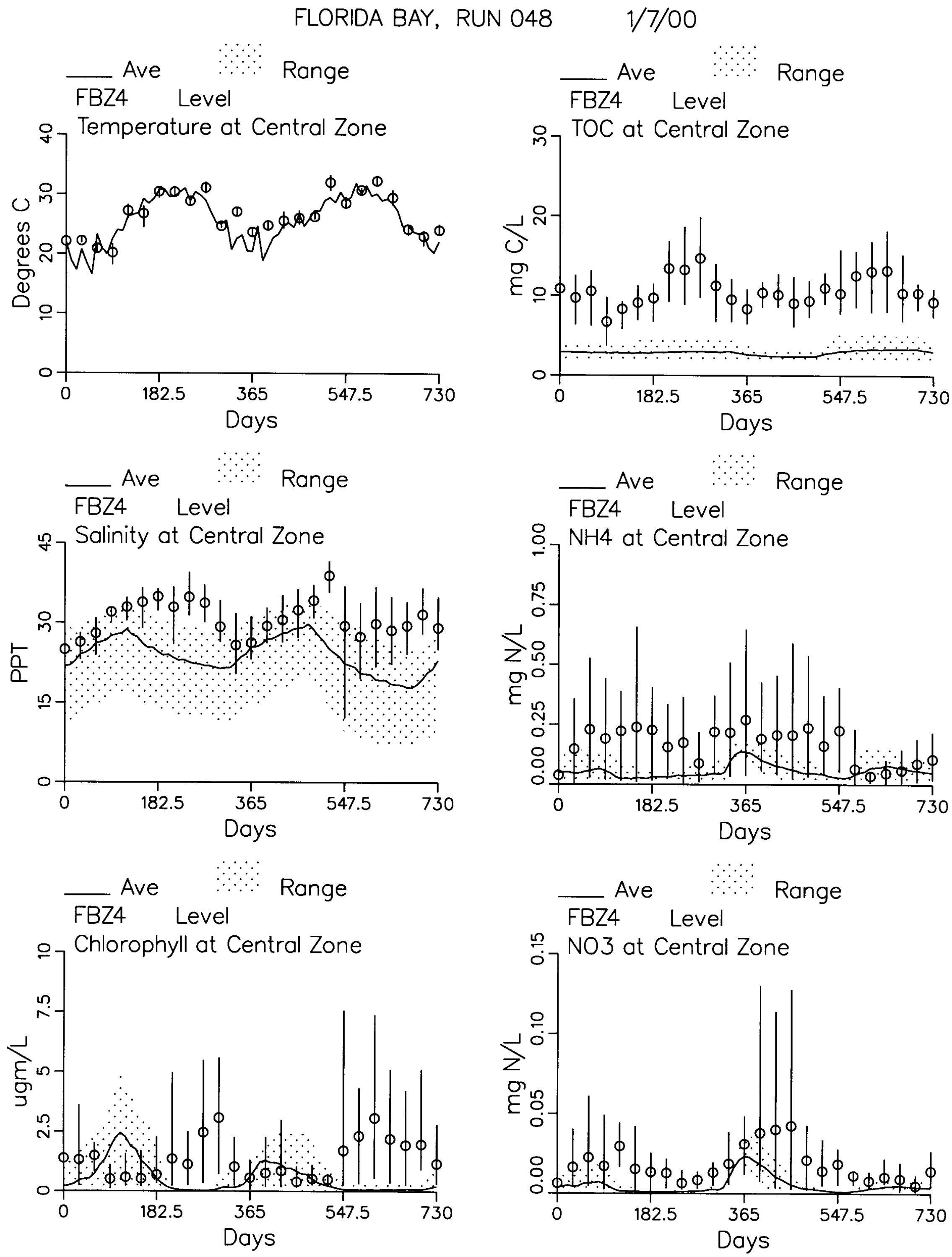

Figure 5.14. Computed and observed water quality in central Florida Bay 1996-1997. Computed mean and range shown as solid line and shading. Observed mean and range shown as open circles and bars.

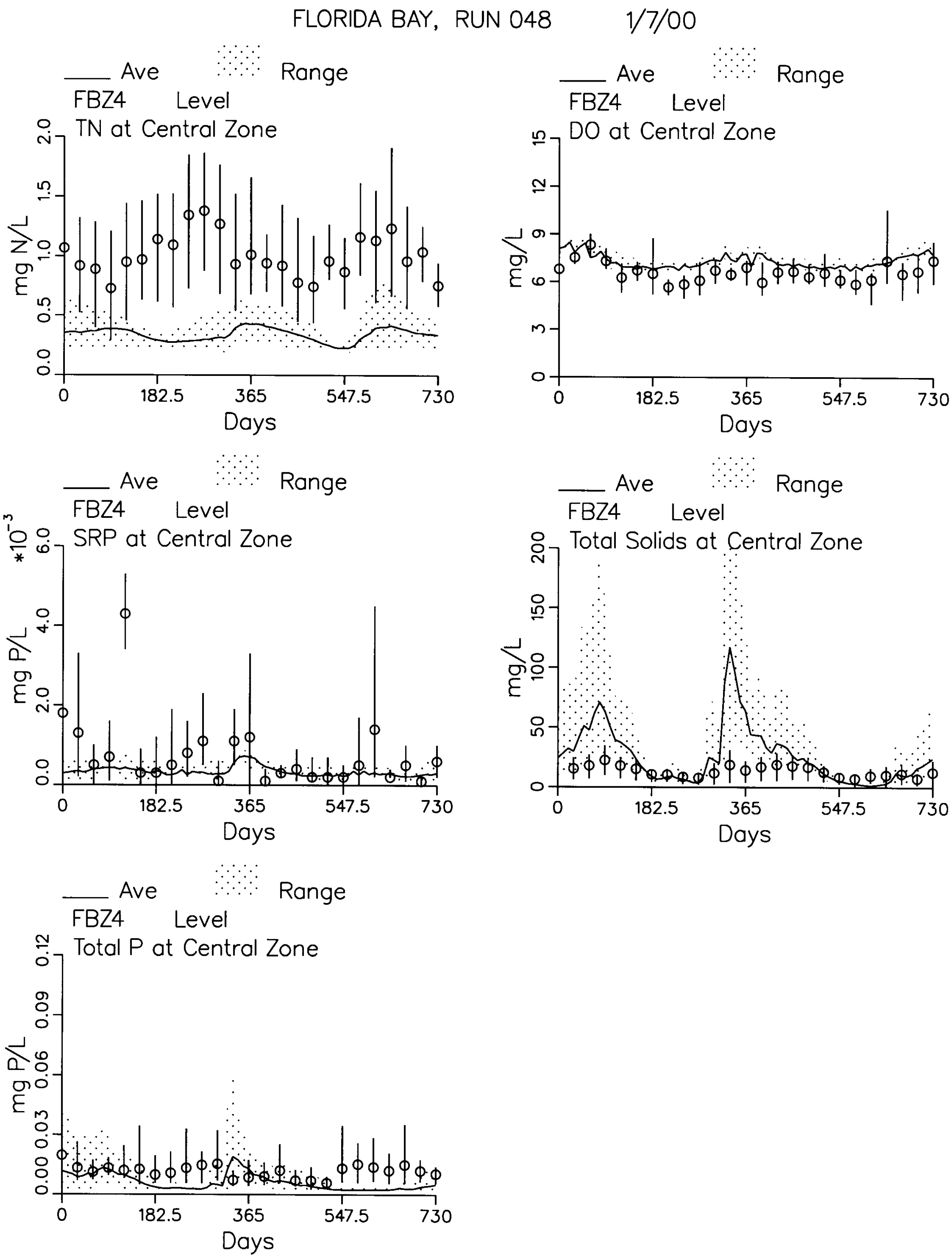

Figure 5.15. Computed and observed water quality in central Florida Bay 1996-1997. Computed mean and range shown as solid line and shading. Observed mean and range shown as open circles and bars.

Interpretation of results from the water quality model was severely compromised by lack of a verified hydrodynamic model operable on the same time scale as the water quality model.

Successful simulation of a ten-year sequence of water quality was virtually impossible without corresponding hydrodynamics. The highest priority should be given to application of a detailed, volume-conservative hydrodynamic model to the bay and adjoining waters. The model should simulate a ten-year period, at least, and provide good agreement to salinities observed within that period.

The major uncertainty in the system nutrient budget is transport across the western boundary and through the Keys passes. This transport cannot be observed on a long-term basis. Computation via a model is the only alternative for long-term budget estimates. High priority should be given to estimating flow across system boundaries once a verified hydrodynamic model is available.

Sensitivity analysis indicates model computations are very sensitive to the biological activity at the sediment-water interface. In the present model, this activity is represented by the benthic algal component. The model, as formulated, cannot represent all observed fluxes, especially of dissolved organic matter. Attention should be devoted to quantifying sediment-water fluxes, to investigating the nature of the benthic community, and to process-based modeling of this community.

A great deal of observations have been collected in the bay since this study commenced and a good deal more is known about the bay than was known a few years ago. Once suitable hydrodynamics are available, the water quality model should be re-applied, on a ten-year time scale, and validated with the latest observations of conditions and processes in the bay. Concurrent with the re-application, first-order improvements (e.g. division of dissolved organic matter into labile and refractory components) can be incorporated into the water quality model.

As part of the Florida Bay and Florida Keys Feasibility Study (of the Comprehensive Everglades Restoration Plan), a new attempt is currently being made to develop, calibrate, validate and apply a Florida Bay water quality model.

Current/Ongoing Research

Unresolved Questions

Past information needs relative to nutrient cycling in Florida Bay were coupled to understanding the factors that triggered the mass mortality of seagrass and what initiated and maintained the phytoplankton blooms. Current needs have become more focused around assessing the impact of various environmental management strategies being considered for Bay restoration. In particular, we need to accurately predict the sensitivity of the Bay's nutrient cycles to changing fresh water flow to the Bay, and the resultant change in the Bay's salinity regime. For much of the Bay, any factor that increases P availability either by increasing sources or decreasing removal is likely to exacerbate the current problems of the Bay. Recent evidence also indicates that algal blooms in the central and western Bay are also stimulated by N enrichment. Thus we need thorough understanding of the Bay's nutrient cycles, particularly with regard to the fate and effects of dissolved organic nitrogen inputs from the Everglades. Questions that the future program should address in order to meet these needs are as follows.

1. What are the sources of nutrients that sustain algal blooms?

Understanding the mechanisms that have triggered and are sustaining algal blooms in the Bay is fundamental to restoration decision-making. This understanding entails quantifying the nutrient demands of these algae and how these nutrients are supplied.

2. How will changing fresh water flow directly and indirectly alter the supply and availability of nutrients in the Bay? What effect does changing salinity have on nutrient availability in the Bay?

- How will the quality and quantity of nutrient outputs from the Everglades change with restoration?
- What is the fate and effect of dissolved organic matter from the Everglades and how will this change with restoration?
- What effect does changing salinity have on nutrient cycling and availability in the Bay?

With increased freshwater flow expected from restoration of the Everglades and Florida Bay, nutrient loading from the Everglades watershed also will probably increase. For nitrogen, most of this loading is in the form of dissolved organic compounds. The sources, fate, and effects of DON from the Everglades watershed are not known. Thus, predictions of how changing freshwater flow will influence these DON dynamics are highly uncertain. Measurements of the composition and bioavailability of Everglades DON to Florida Bay’s microbial communities (pelagic, epiphytic, and benthic) are essential in order to assess the functional relationship of Florida Bay and its watershed. While the magnitude of this expected increase is unknown, this direct input may be less important than the indirect effect of an altered salinity regime caused by increased freshwater influx. Altered salinities can affect internal nutrient cycling by: (1) altering community structure, such as changing seagrass species dominance, thus changing nutrient storage and cycling, and (2) modifying specific processes, such as P surface reactions and sulfate reduction.

Changing freshwater flow may also indirectly affect nutrient availability in the Bay. Altered salinity can affect internal nutrient cycling by: (1) altering community structure, such as changing seagrass species dominance, thus changing nutrient storage and cycling; and (2) modifying specific processes, such as P surface reactions and sulfate reduction. Changing freshwater flow and salinity could also alter nutrient processing in the mangrove zone and thus alter nutrient exchange along the Bay's northern boundary, the Gulf of Mexico boundary with the Everglades, and near mangrove islands in the Bay.

The factors that influence the loading of nutrients into Florida Bay, and the availability of nutrients within the Bay are not well understood. In particular, we need to understand the effect that potential environmental management actions, such as increasing fresh water flow and decreasing salinity, will have on the Bay's nutrient transformations and fluxes. Information on suspended sediment particles and on factors that may influence the mobilization and immobilization of P in carbonate sediments is critical. Results of past experiments (Zhang et al. 1999) need to be evaluated in the context of water quality model development to assess the sufficiency of current data for estimating salinity effects.

Given the unusually high ammonium concentrations of the Bay and the potential for N limitation the western Bay, experiments on factors that may influence key N transformations, such as nitrification and denitrification are also needed. Experiments that explore how nutrient cycling is altered by changing seagrass community structure and physiological condition (particularly below-ground nutrient changes) are also important, but are yet to be done.

3. What effect does a change in seagrass community structure have on nutrient availability in the Bay? Has seagrass mortality only increased nutrient availability by releasing nutrients from this detrital source, or has seagrass mortality also caused other less direct changes, such as a decrease in the capacity of the sediments to sequester nutrients?

The lag of several years between the onset of seagrass mass mortality and the occurrence of algal blooms in the Bay argues against the hypothesis that only nutrients released from dead seagrass tissue fuel the blooms. However, the increase in nutrients from this detrital source, combined with a net decreased uptake capacity associated with seagrass mortality, may explain the bloom's temporal patterns. Thus, estimates are needed of net benthic nutrient uptake or release rates, over a range of seagrass growth rates, mortality rates, and detrital decomposition rates for different seagrass species. The accuracy of such estimates may largely depend upon understanding sedimentary nutrient transformations, including how seagrass roots affect nutrient mobility and how such processes change with seagrass mortality. Additionally, seagrass mortality may have indirectly affected nutrient cycles in the Bay. For example, sediment resuspension increases with decreasing seagrass density, and P associated with this suspended sediment may be available to phytoplankton. Finally, changing seagrass cover also influences the biomass and activity of benthic algal mats. This change in microbial mats in turn affects nitrogen availability by altering patterns of nitrification, denitrification, and nitrogen fixation. Measurements of the quantitative relationships of these processes with algal and SAV community structure are needed.

Given the shallow depth and restricted circulation of Florida Bay, internal cycling and transformations of nutrients probably have a strong influence on the structure and productivity of Bay communities. These nutrient pathways and transformations have not been well studied. Essential measurements include nutrient uptake by primary producers (especially seagrass and phytoplankton), the exchange of nutrients between the sediments and the water-column, the diagenesis of nutrients within the sediments (especially P - carbonate reactions and N transformations), and microbial and inorganic reactions within the water column (such as nitrification and P sorption to, and removal, from suspended sediment).

4. How do we deal with the spatial heterogeneity of internal nutrient cycling in the Bay?

There is no unified field theory for ecology; process rates from one area may not be applicable for another. What other factors are important in driving these processes?

5. What is the quantitative role of microphytobenthos in nutrient cycling and how is this likely to change with Everglades restoration?

The microphytobenthos has been shown to be influential in regulating benthic flux rates. Fluxes in the form of drift seagrasses and algae have not been determined.

6. To what extent is atmospheric deposition of nutrients contributing to ecological changes in Florida Bay? What is temporal variability (including long-term trend) of this nutrient source?

Atmospheric inputs have been shown to be a significant component of external nutrient loading, especially N. There are no estimates of long term trends in atmospheric nutrient loading at present.

7. Is ground water an important nutrient source in Florida Bay? If so, what is the spatial and temporal pattern of this input?

Given the high nutrient content of ground waters beneath most of the Bay, any groundwater flux approaching recently published rates (about 1 cm d^{-1}) would result in a very high nutrient flux. The accuracy of these estimates should be checked - sites with significant upward groundwater advection should be identified and, if found, nutrient concentrations at these sites should be measured.

Summary of Ongoing Research

1. Continued monitoring of ambient water quality in Florida Bay
2. Continued monitoring of freshwater inflows and loads with expansion of network along Florida Bay and southwest Florida/Gulf coast beginning
3. Continued monitoring of coastal circulation and biological and chemical parameters, with interpretation of transport and exchange of South Florida coastal waters
4. Expanded research into nutrient cycling in wetland/mangrove areas and seagrasses/epiphytes
5. Study of carbonate system - P - Fe relations
6. Characterization of chemical structure of organic C and N from wetland/mangrove areas
7. Assessment of microbial bioavailability of organic C and N from wetland/mangrove areas
8. Expanded measurements of benthic nitrogen fixation, nitrification, and denitrification rates
9. Measurements of phytoplankton N uptake rates
10. Quantification of microbial loop parameters: heterotrophic bacterial numbers, bacterial production, nanoflagellate/protist grazing rates, and phytoplankton primary production
11. Effects on the coastal Everglades ecosystem of variability in regional climate, freshwater inputs, disturbance, and perturbations
12. Development of N and P mass balance models and measurements of nutrient cycling rates in Florida Bay
13. Assessment and monitoring of dissolved N in Florida Bay
14. Measurement of nutrient fluxes through Florida Keys passes
15. Monitoring of salinity and estimates of fluxes of water, TN, and TP across the southern Everglades mangrove zone
16. Development of an integrated hydrodynamic and water quality model to evaluate relationships with freshwater flow and oceanic/Gulf hydrodynamics and exchange is in a planning phase

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