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## TOTAL AMMONIA CONCENTRATIONS IN SOIL, SEDIMENTS, SURFACE WATER , AND GROUNDWATER ALONG THE WESTERN SHORELINE OF BISCAYNE BAY WITH THE FOCUS ON BLACK POINT AND A REFERENCE MANGROVE SITE

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### **EXECUTIVE SUMMARY**

This study focused on ammonia as a potential stressor of marine benthic communities in Biscayne Bay but also included other nutrients as well. The specific tasks included in this project were: 1) Black Point Monitoring Program, 2) Black Point Monitoring Comparison, 3) Shoreline Nutrient Survey, 4) Shoreline Benthic Community Survey, and 5) Mangrove Transect Comparison.

The Black Point Monitoring Program showed that nutrient concentrations (especially ammonium were elevated in the canals adjacent to the landfill. The median value of unionized ammonia at Station 12 was 122 ppb which may be toxic to some marine fish. However, the very low dissolved oxygen at the same site would also preclude much marine life from thriving in this area.

The Black Point Monitoring Comparison was performed by statistical comparison of data from 1993 surveys with this study. No differences in water quality in the canals or nearshore area were found. We can clearly say that there has been no measurable improvement in water quality between surveys.

The Shoreline Nutrient Survey showed that ammonium concentrations were highest in the nearshore waters off Black Point, the Cutler Channel, and the Mowry Canal area. A very different distribution was observed for nitrate where highest concentrations were found off the Cutler Channel and very low levels found in the nearshore waters between Cutler Channel and Goulds Canal. A hot spot in total phosphorus was observed off Mangrove Key in extreme south Biscayne Bay. Another interesting aspect was the correspondence between sediment and water column nutrient levels. Levels of ammonium in the sediments are approximately an order of magnitude higher than the water column and generally follow each other. This was also true for total phosphorus although the concentrations in sediment and water were different by only a factor of 3.

Shoreline Benthic Community Survey resulted in the classification of 5 angiosperms and 22 algal species. Among the angiosperms, Thalassia testudinum and Halodule wrightii, were the most common. Thalassia and Halodule did not share the same distribution or abundance patterns from north to south - small amounts of Halodule were found throughout the study area with a general increase in abundance from south to north. The inverse was true with Thalassia abundance, which generally increased in abundance in the southerly direction. A break in Thalassia distribution occurred at the Goulds Canal/Black Point Area. For several km south, no Thalassia was reported but abundant Halodule was found in its place along with unknown green species, brown algae, and other noncalcareous green species. The break in Thalassia cover may have been partly due to salinity. Salinity during the survey increased dramatically from north to south, however, highest Thalassia densities occurred in the areas experiencing hypersaline conditions. Variability in salinity may have been important to mortality of *Thalassia* but salinity in the area between Goulds and Military Canals is not as variable as it is off the Mowry Canal. The only other water quality variable which may have influenced *Thalassia* was ammonium. The nearshore area between Goulds and Military Canals has the highest concentrations of ammonium in the water column and sediments of any site in this study. Our results indicate a strong correlation between elevated ammonium concentrations with 1) decreased abundance of Thalassia, 2) increased abundance of Halodule and fast growing algae species, and 3) the increase in filamentous algal cover.

The Mangrove Transect Comparison showed that the mangrove fringe was a source of total phosphorus and possibly some ammonium to the Bay, but not as much as suspected. The Bay itself was a source of nitrate to the mangrove fringe.

Understanding: 1) nutrient concentration spatial and temporal distributions, 2) the relationship between ammonia concentration and the level of benthic community degradation, and 3) the relative significance of natural nutrient addition to the system from anthropogenic or additional loading is paramount to establishing pollution load reduction goals. This project focused on the first two needs listed above to begin to establish a data base for the calculation of load and sources of load to Biscayne National Park.

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#### INTRODUCTION

Biscayne Bay is a shallow subtropical lagoonal estuary located on the southeast coast of Florida. The Bay is situated as a topographic basin on the surface of the Miami Limestone which outcrops to the west of the western shoreline forming a coastal ridge. Biscayne Bay is separated from the Atlantic Ocean by a series of barrier islands and limestone keys cut by shallow tidal passes. Biscayne Bay originated ~6,000 ybp as sea level rose during the Holocene transgression and has increased to a maximum depth of ~4 m during that time. The N-S orientation and different coastal morphology allow the Bay to be separated into three distinct regions: North, Central and South Bay (Card Sound). North Bay is a highly urbanized system. Channel dredging, the construction of Haulover Cut, and the extensive enlargement of Government Cut has altered circulation patterns resulting in increased salinity in this zone.

The western shore of Central Bay (Dinner Key to Turkey Point) was originally composed of a mangrove fringe and extensive freshwater marshes reaching to the foot of the coastal ridge several miles inland. These freshwater marshes were maintained by local rainfall and Everglades discharge via the transitional glades. After the turn of the century the transverse glades were channeled and drained directly into Biscayne Bay which resulted in saltwater encroachment. This was identified by the early 1940's and control structures and a coastal storm protection levee (L-31E) were constructed. The L-31E canal and levee system eliminated all sheet flow to Central and South Biscayne Bay. Canal water now enters the Bay as a point source and contains high levels of urban and agricultural waste creating a nutrient loading and time of delivery problems in the ecosystem. South Bay is relatively isolated from urban development, with the exception of Turkey Point Power Plant facility. Although this region has historically received less freshwater runoff than other areas of the Bay, it has also seen the greatest decline in freshwater inputs due to construction of the L-31E levee and US 1.

Biscayne National Park is located adjacent to large population and agricultural centers of Miami-Dade county. Over the past 100 years of land development, Biscayne Bay circulation patterns have been highly altered by management activities. Freshwater sheet flow discharge was replaced by channelized discharge via canals which radically changed the quantity, timing, and distribution of input to the Bay (Alleman et al. 1995). Because of this management activity, the estuarine zone of Biscayne Bay has been much reduced.

In conjunction with the changes in quantity, timing, and distribution of freshwater there have been changes in quality of the input. The water quality of both canal and groundwater inputs has declined as urbanization and agriculture have become more pronounced across the landscape. Numerous landfill and contaminated sites impact the groundwater that enters Biscayne Bay (Meeder et al. 1997). Nutrient loading estimates from the Mowry Canal to Biscayne Bay are very high compared to the typically low levels (oligotrophic conditions) found in other areas (Meeder et al. 1997). The addition of groundwater nutrient inputs to the model suggests that Biscayne Bay may be undergoing considerably more nutrient loading than previously thought (Meeder et al. 1997). This poses not only an environmental degradation problem but one of potential ammonia toxicity. As a consequence, the nearshore aquatic environment has displayed symptoms of decreased primary productivity and offshore migration of desirable benthic communities (Meeder et al. 1997).

This study focuses on ammonia as a potential stressor of marine benthic communities. Coastal mangroves are highly productive systems that are known to export ammonia because of microbial  $N_2$  fixation associated with aerial roots (Boto and Robertson 1990) and anaerobic decomposition processes (Peligri and Twilley 1999). Ammonia production in the coastal mangrove system is limited to a fraction of the biomass turnover on an annual basis and is therefore fixed within rather narrow bounds at any site (Boto and Robertson 1990; Lara and Dittmar 1999). In addition, most mangrove swamps along the western shore of Biscayne Bay grow in carbonate marl soil, about 1 m thick, which overlies the bedrock (and groundwater). This mud layer is relatively impermeable and separate the surficial interstitial soil and tidal water from the terrestrial groundwater from the watershed. This means that ammonia derived from inner mangrove forests is separate from anthropogenic derived ammonia in groundwater until they discharge into the Bay. An exception to this may be the thin fringing mangrove zone along the waters edge which frequently are not underlain by the marl soil horizon. This is the zone of highest productivity, greatest physical export of detritus, greatest belowground biomass production (actually accretion), and soils with the best gas exchange.

Groundwater nutrient levels obtained 50 m from shore along Biscayne Bay from the Dinner Key to Mowry Canal have total ammonia concentrations 30 or more times greater than those of overlying surface waters (Meeder et al. 1997). In addition, highest groundwater concentrations were found at Black Point and decreased by nearly half both northwards and southwards (Meeder et al. 1997). The location of the highest concentrations off Black Point was no surprise because the site is located close to the old and present Dade County landfills.

Only limited data on Biscayne Bay ammonia concentrations is available for inshore areas. The need to understand the distribution of ammonia in Biscayne National Park is necessary to establish pollution guidelines based upon real spatial and temporal distributions and their impacts to Bay ecology. A restudy of the Black Point area will aid in the determination if remedial environmental protection activities at the landfill have succeeded in lowering the nutrient concentrations delivered to the Bay. Comparisons between the Black Point area and the mangrove reference site should also aid the Park in determining the background levels of ammonia expected from coastal mangroves in contrast to ammonia levels associated with anthropogenic activities.

The specific tasks included in this project were:

- Task 1 Black Point Monitoring Program
- Task 2 Black Point Monitoring Comparison
- Task 3 Shoreline Nutrient Survey
- Task 4 Shoreline Benthic Community Survey
- Task 5 Mangrove Transect Comparison

The Black Point Monitoring Program (Task 1) was designed to produce a monthly characterization of nutrient concentrations in the receiving waters surrounding the landfill. Comparisons between previous (Jones 1994) and current nutrient levels at Black Point (Task 2) indicated if remedial activities for the protection of the Bay from excess nutrient loading have been successful.

The purpose of the Shoreline Nutrient Survey (Task 3) was to produce a high resolution map of ammonia along the western BNP shoreline and to point out any hot spots within the mangroves, surface water, and marine sediments. This data was then combined with the ongoing Biscayne Bay Water Quality Monitoring Program operated by SERC and funded by SFWMD to produce a more generalized "snapshot" of nutrient levels in the Bay.

The concurrent Shoreline Benthic Community Survey (Task 4) was designed to provide a high resolution map of plant community structure along the west coast. Comparisons between benthic community characteristics and ammonia levels in water and sediments were proposed to develop an impact gradient curve of the relationship between ammonia levels and degree of community degradation. Documentation of the distribution of ammonia levels and their impacts on the benthos would then be used in the development of non-degradation criteria for BNP waters.

The comparison of mangroves at Black Point and the reference site (Task 5) is designed to determine whether there is a difference between ammonia levels found in natural and impacted areas. The transect data will provide a source gradient by which we can calculate the relative magnitude of ammonia input to the system via mangrove fringe.

### **METHODS**

#### Task 1 - Black Point Monitoring Program

The Black Point Monitoring Program was conducted monthly for one year at six canal surface water sample sites and two terrestrial sites (Fig 3). Most of these sites were the same as those sampled in the previous Black Point study (Jones 1994) in order to allow a direct comparison between data sets (Task 2). The purpose of this component is to determine the magnitude and extent of any ammonia source gradient from the landfill site. In addition, two soil sites were established along the east side of the landfills, on separate sides of the canal.

We decided to measure other nutrient variables along with ammonium in order to ascertain if the landfill had an impact on them as well. This decision was made with best science in mind. However, because of the increased costs, we were restricted to conducting only one shoreline ammonia and benthic survey instead of the proposed two.

Surface and bottom salinity (psu) and temperature (°C) were measured using a combination salinity-conductivity-temperature probe (Orion model 140). Dissolved oxygen (DO, mg  $l^{-1}$ ) was measured 10 cm below the surface using an oxygen electrode (Orion model 840) corrected for salinity and temperature.

Water samples were collected in sample-rinsed HDPE bottles using standard SERC procedures. Interstitial water of soils and sediments for the Shoreline Nutrient Survey were collected by vacuum lysimeter. Soil and sediment were collected by coring. Duplicate, unfiltered water samples were collected using 3x sample rinsed 120 ml HDPE bottles for analysis of total constituents. Duplicate water samples for dissolved nutrients were collected using 3x sample rinsed 150 ml syringes which were then filtered by hand through 25 mm glass fiber filters (Whatman GF/F) into 3x sample rinsed 60 ml HDPE bottles.

Unfiltered water samples were analyzed for total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), total silicate (Si(OH)<sub>4</sub>), and turbidity. TOC was measured by direct injection onto hot platinum catalyst in a Shimadzu TOC-5000 after first acidifying to pH<2 and purging with CO<sub>2</sub>-free air. TN was measured using an ANTEK 7000N Nitrogen Analyzer using O<sub>2</sub> as carrier gas to promote complete recovery of the nitrogen in the water samples (Frankovich and Jones 1998). TP was determined using a dry ashing, acid hydrolysis technique (Solórzano and Sharp 1980). TS was measured using the molybdosilicate method (Strickland and Parsons 1972). Turbidity was measured using an HF Scientific model DRT-15C turbidimeter and reported in NTU.

Filtrates were analyzed for soluble reactive phosphorus (SRP), nitrate+nitrite (NO<sub>x</sub>), nitrite (NO<sub>2</sub><sup>-</sup>), and total ammonia (NH<sub>4</sub><sup>+</sup>) on a four channel autoanalyzer (Alpkem model RFA 300). All analyses were completed within 28 days after collection (except for NH<sub>4</sub><sup>+</sup>, which was run the following day) in accordance to standard SERC laboratory quality control guidelines.

Some parameters were not measured directly, but were calculated by difference. Nitrate  $(NO_3^{-2})$  was calculated as  $NO_X^{-} - NO_2^{-}$ , dissolved inorganic nitrogen (DIN) as  $NO_X + NH_4^{+}$ , and total organic nitrogen (TON) defined as TN - DIN. All concentrations are reported as ppm-N or P unless noted. All elemental ratios discussed were calculated on a molar basis.

#### Task 2 - Black Point Monitoring Comparison

Data from Jones (1994) and current programs were compiled and analyzed by station using the Mann-Whitney U test; the nonparametric version of the two group unpaired *t*-test. Significance was set at P < 0.05.

#### Task 3 - Shoreline Nutrient Survey

During the 1998 dry season, nutrient concentrations in nearshore surface water (~50 m offshore), marine sediment pore water (~50 m offshore), mangrove soils (~25 m onshore), and mangrove surface waters (~25 m onshore) were sampled approximately every 1 km along the west shoreline for a total of 22 (Fig 2). We also sampled near canal mouths and at significant features. Data from the Shoreline Nutrient Survey were combined with data from the FIU water quality monitoring program for Biscayne Bay. All data was collected in the same month and presented as kriged contour plots (Surfer, Golden Software).

#### Task 4 - Shoreline Benthic Community Survey

The Shoreline Benthic Community Survey was conducted in conjunction with the Shoreline Nutrient Survey. Benthic plant community structure was characterized in three plots  $(0.25 \text{ m}^2)$  within one meter of each Shoreline Ammonia Survey sampling site. The number of shoots of marine plants was counted, measured, and weighed in subplots within each of the three plots. Plant taxa and their abundance were recorded using the Braun-Blanquet survey method (Fourqurean et al. 2000). Species presence, percent cover, and community structure along with distance from shore, water depth, soil depth and type, salinity, and other parameters was also recorded. Epiphyte percent cover was recorded on the larger plant leaves and bay bottom at each plot. Data were analyzed by standard methods employed in earlier studies (Meeder et al. 1997).

#### Task 5 - Mangrove Transect Comparison

The Mangrove Transect Comparison was structured so as to provide information concerning nutrient inputs from mangrove forests in Biscayne Bay. The sampling area was selected based upon several criteria: 1) low range of ammonia concentration, 2) lack of known anthropogenic source of ammonia, and 3) similar type mangrove system as found at Black Point (narrow fringe with wide basin). Five sites were sampled: a upstream mostly freshwater distribution canal (DC) which was 640 m west of the coast and 300 m north of the Mowry Canal; a site east of DC in the mangrove fringe (TF); a site just offshore TF (TBB); a mangrove fringe site 500 m south of the Military Canal (CF); and a corresponding offshore site (CBB). At each site, surface water and soil or sediment were sampled and analyzed for nutrients as above on a monthly basis for one year.

#### RESULTS

Task 1 - Black Point Monitoring Program

Summary of results from the monthly Black Point Monitoring Program are shown in Table 1. For the period of record, salinity ranged from 0.02 - 39.7 psu; temperature from 20.9 - 31.6 °C, DO from 0.2 - 11.4 mg l<sup>-1</sup>, pH from 6.90 - 8.78, NH<sub>4</sub><sup>+</sup> from 0.004 - 26.97 ppm, and NH<sub>3</sub> from 0.0 - 654 ppb. Additional nutrient values also showed large ranges: NO<sub>3</sub><sup>-2</sup> from 0.002 - 0.415 ppm and TP from 0.002 - 0.94 ppm. These large ranges are indicative of terrestrial/groundwater nutrient loading to the canals and inshore areas of Biscayne Bay.

Monthly maps of  $NH_4^+$  concentration plotted by station are presented in Figs. 3-14. Concentrations are on log scale because the range in data was so large. Highest  $NH_4^+$  concentrations routinely occurred at Sta #12 which is directly downstream of the landfill. Sta. #12 also had highest DOC,  $NO_2^-$ ,  $NH_3$ , SRP, and lowest DO levels. The median value of  $NH_3$  at #12 was 122 ppb which may be toxic to some marine fish. However, the very low DO at the same site would also preclude much marine life from thriving in this area.

Differences among stations were shown as box-and-whisker plots (Fig. 15 & 16). The boxand-whisker plot is a powerful statistic which displays the median, range, and the shape of the data distribution. Water quality variable distributions are usually skewed to the right (nonnormal) so it is more appropriate to use the median as the measure of central tendency. The central, horizontal line of the box is the median of the data, the top and bottom of the box are the 25th and 75th percentiles (quartiles), the ends of the whiskers are the 10th and 90th percentiles, and any points outside (<10th and >90th percentiles) may be considered outliers (suppressed in the graphs). The box-and-whisker plot also serves as a graphical, nonparametric ANOVA. The notch in the box is the 95% confidence interval of the median. When notches among boxes do not overlap, the medians may be considered significantly different.

Comparing the canal sites (#10, 11, 12, & 13) to the nearshore sites (#14 & 15) it becomes clear that the nearshore sites have higher salinity, pH, and a narrower range in nutrients. We should point out that station #14 was located in the water column above two groundwater wells in ~1 m of water. Water quality at this site may have been influenced by seepage from these wells as they had positive hydraulic pressure at all times of sampling. The shallow well had significantly higher NO<sub>3</sub><sup>-2</sup> and lower salinity than the deep well (data not shown). From this we may imply that groundwater in the shallow well was derived more from surface water than the deep well, which has been previously confirmed by Meeder et al. (1997). Both wells had significant amounts of NH<sub>4</sub><sup>+</sup> present; generally an order of magnitude greater than un-impacted surface waters.

#### Task 2 - Black Point Monitoring Comparison

Statistical comparison of data from 1993 surveys with this study resulted in no significant difference (P>0.05) in water quality variables in the canals or nearshore (Fig. 17-20). Each station was treated separately using a Mann-Whitney U test; the nonparametric version of the two group unpaired *t*-test. What was noticeable was that the ranges in the data of the current study were larger than found in the previous study. This was probably the result of climactic influence such as higher rainfall in 1998-99. We can clearly say that there has been no measurable improvement in water quality between surveys.

Task 3 - Shoreline Nutrient Survey

This survey was conducted in April 1998 which happened to occur at the end of a very dry season. Salinity in southern Biscayne Bay was elevated in both nearshore and offshore areas (Fig. 21) as a result of this. Ammonium concentrations (Fig. 22) during this period were highest in the nearshore waters off Black Point (0.035 ppm), the Cutler Channel (0.148 ppm), and the Mowry Canal area (0.013 ppm). NH<sub>3</sub> was also elevated in these areas (Fig. 23) being 3.6, 2.4, 3.1 ppb, respectively. A very different distribution was observed for NO<sub>3</sub><sup>-2</sup> (Fig. 24) with highest concentrations being found off the Cutler Channel (0.148 ppm) and very low levels found in the nearshore waters between Cutler Channel and Goulds Canal. A hot spot in TP (0.0519 ppm) was observed off Mangrove Key in extreme south Biscayne Bay (Fig 25). Otherwise, TP concentrations were very low (<0.015 ppm) throughout the Bay. TOC (Fig. 26) and TON (Fig. 27) showed similar high nearshore – low offshore gradients. Highest TOC (12.2 ppm) and TON (1.6 ppm) concentrations occurred off the mangroves between Cutler Channel and Goulds Canal. There was also a local increase in TON between Goulds and Military Canals.

Another interesting aspect of the Shoreline Nutrient Survey was the correspondence between sediment and water column nutrient levels. Figure 28 shows the  $NH_4^+$  concentration in water and sediment along the coast from north to south. Levels of  $NH_4^+$  in the sediments are approximately an order of magnitude higher than the water column and generally follow each other. This was also true for TP (Fig. 29) although the concentrations in sediment and water were different by only a factor of 3.

Interestingly, the area around Black Point which showed high  $NH_4^+$  from the landfill had a corresponding depression in TP. This may be because of increased biological demand for P from the external supplement of N.

#### Task 4 - Shoreline Benthic Community Survey

Table 2 is a list of marine plant taxa reported in this study. Taxa were included only when found in more than three separate plots or if they occupied more than 2% of the area in a single plot. This criteria excluded numerous uncommon species that carry little ecological information at the community level supported by literature. Five angiosperms and 22 algal species were recorded. Filamentous algae were not further classified. Among the angiosperms, Thalassia testudinum and Halodule wrightii, were the most common, the others being found only at a few stations. Thalassia and Halodule, although abundant at most sites, did not share the same distribution or abundance patterns from north to south (Fig. 30). Minor amounts of Halodule were found throughout the study area with a general increase in abundance from south to north. The inverse was true with Thalassia abundance, which generally increased in abundance in the southerly direction. The red algae group was also more abundant in the south. *Penicillus* and most other calcareous green species displayed the same distributional pattern as Thalassia. Some fast growing green algae species (Acetabularia) did not exhibit obvious trends in distribution or abundance. Filamentous algae was not taxonomically subdivided further but was reported as percent cover as an epiphyte. Generally, either filamentous algae cover was low (less than 20%) of available substrate) or significant (over 80% of available cover). Filamentous algae cover was highest in the area between Black Point and the Mowry Canal with minor hot spots located near other canal mouths.

A break in *Thalassia* distribution occurred at the Goulds Canal/Black Point Area. For several km south, no *Thalassia* was reported but abundant *Halodule* was found in its place (Fig. 29).

The break in *Thalassia* was also associated with changes in distribution of other marine plants. An unknown green species, brown algae, and other noncalcareous green species increased in abundance where *Thalassia* was not present.

The break in *Thalassia* cover may have been partly due to salinity. Salinity during the survey increased dramatically from north to south (Fig. 31), however, highest *Thalassia* densities occurred in the areas experiencing hypersaline conditions. Variability in salinity may have been important to mortality of *Thalassia* but salinity in the area between Goulds and Military Canals is not as variable as it is off the Mowry Canal (Boyer, unpublished data). The only other water quality variable which may have influenced *Thalassia* was  $NH_4^+$  (Fig. 32). The nearshore area between Goulds and Military Canals has the highest concentrations of  $NH_4^+$  in the water column and sediments of any site in this study. It was more likely that chronic inputs of  $NH_4^+$  were responsible for *Thalassia* loss.

#### Task 5 - Mangrove Transect Comparison

Data were analyzed using the nonparametric Mann-Whitney U Test which is comparable to an unpaired *t* Test. Some general trends were observed which are best visualized in Fig. 33. The distribution channel (DC) was not a source of  $NO_3^{-2}$ ,  $NH_4^+$ , TP, or SRP to the mangroves. However, DC was a significant source of Chl *a* and TOC to the mangrove fringe. The mangrove fringe itself was a source of TP, SRP, and possibly  $NH_4^+$  to the Bay. The Bay itself was a source of  $NO_3^{-2}$  to the mangrove fringe.

Nutrient concentrations in the mangrove fringe sites (TF and CF) were not significantly different from each other (P>0.10) so they could be pooled and treated as being representative of the mangrove fringe in Biscayne Bay. However, we did not do this as the Bay sites had some significant differences –  $NH_4^+$  and TOC were slightly higher at CBB and  $NO_3^{-2}$  was lower. Most important was the finding that although  $NH_4^+$  concentrations are high in mangroves, a significant portion of that may be derived from upland drainage.

## DISCUSSION

The Black Point Monitoring Program showed that nutrient concentrations (especially ammonium were elevated in the canals adjacent to the landfill. The median value of unionized ammonia at Station 12 was 122 ppb which may be toxic to some marine fish. However, the very low dissolved oxygen at the same site would also preclude much marine life from thriving in this area.

The Black Point Monitoring Comparison was performed by statistical comparison of data from 1993 surveys with this study. We found no difference in water quality in the canals or nearshore area between the two studies. From this we can clearly state that there has been no measurable, beneficial effect of remediation activities on the water quality of the Black Point area.

The Shoreline Nutrient Survey showed that ammonium concentrations were highest in the nearshore waters off Black Point, the Cutler Channel, and the Mowry Canal area. A very different distribution was observed for nitrate where highest concentrations were found off the Cutler Channel and very low levels found in the nearshore waters between Cutler Channel and Goulds Canal. A hot spot in total phosphorus was observed off Mangrove Key in extreme south Biscayne Bay. Another interesting aspect was the correspondence between sediment and water column nutrient levels. Levels of ammonium in the sediments are approximately an order of magnitude higher than the water column and generally follow each other. This was also true for total phosphorus although the concentrations in sediment and water were different by only a factor of 3.

Submerged aquatic plant communities respond to nutrient loading by the replacement of slow growing with faster growing species and finally by phytoplankton (Duarte 1995). In many South Florida water bodies heavy epiphytic algae growth replaces phytoplankton, with the same end result. In many cases, the indirect effect of faster growing species dominance is additional stress on the slower growing species by shading or light exclusion (Orth and Moore 1983). *Thalassia* is replaced by *Halodule* in seagrass areas with increases nutrient loading (Powell et al 1991; Fourquerean et al 1995). In other studies *Zostera marina* and *Ruppia* were replaced by faster growing green algae species

The distribution of *Thalassia* and other aquatic vegetation have been linked to groundwater discharge in Biscayne Bay (Kohout and Kolipinski 1967; Meeder et al 1996) and other regions such as Yucatan, Mexico (Herrera-Silveira 1994) and Australia (Johannes 1980). Meeder et al (1997) found that *Thalassia* was not abundant in areas receiving groundwater discharge. This area was from the shoreline to 400 m offshore in the area between the Military and Mowry Canals. Benthic community distribution influenced by groundwater discharge usually form bands parallel to the shoreline and the effects of groundwater discharge usually decrease exponentially with distance offshore. However, the major source of western Biscayne Bay nutrient loading is canal discharge.

Canal discharge varies more in both nutrient concentration levels and discharge volumes seasonally than does groundwater. Because most canal discharge occurs during the rainy season with prevailing southerly or southeasterly winds canal waters most frequently pile up along the western shore of Biscayne Bay. Therefore low salinity, nutrient rich canal water is held along the shoreline. The effects of this pattern of freshwater canal discharge is hard to separate from the groundwater discharge pattern in terms of nearshore benthic community structure and

productivity (Meeder et al 1997). The nutrient loading of both canal and ground water is significant.

Although ammonia toxicity or increased nutrient concentration may be responsible for the lack of *Thalassia* and slower growing algae species in the vicinity of Black Point our data does not unequivocally support this relationship. Our data does support a more than causal relationship between high  $NH_4^+$  concentration with the lack of *Thalassia*, however, the nutrient levels may be a surrogate of other causes. For example, both high  $NH_4^+$  and nutrient concentrations are related to freshwater delivery to the bay via canal and groundwater, which may carry other agents acting alone or synergistically with  $NH_4^+$  and nutrients to cause toxic or unfavorable conditions for *Thalassia* and other slow growing plants. In addition, salinity characteristics may also play a role in *Thalassia* competition.

*Thalassia* responds best to normal marine salinities. Salinities too high or too low or a rapidly changing salinity regime produce stress to *Thalassia* that frequently favors other species. Historically the northern portion of Biscayne Bay was much more estuarine in nature but has maintained near marine salinities since the opening of Haulover Cut and dredging of Miami River-Government Cut Channels which permit rapid freshwater discharge mixing and export. Northern Biscayne Bay also has more frequent high turbidity periods which affects light availability, especially in deeper portions of the Bay (Harlem 1979). The southern part of the Bay is less well flushed, perhaps, but has much less freshwater discharge. This is especially true south of North Canal. In this region salinities are always near marine conditions and can become slightly hypersaline during extended dry periods such as during our April sampling period. Normally *Thalassia* abundance increases from north-to-south because of more continuous near marine salinity and low turbidity levels in Southern Biscayne Bay. This trend is apparent when plotting salinity vs *Thalassia* abundance (Fig. 30). The break in the trend is obviously not soley the result of salinity.

The major purpose of the funding for this project was to determine if  $NH_4^+$  levels were elevated enough in the waters and soils of nearshore Biscayne Bay to produce toxic affects on *Thalassia*. Previously the relationship between *Thalassia* distribution and salinity and nutrient concentrations were discussed with the conclusion that the competitive advantage of fast growing species over slow growing species and the resulting light competition can adequately explain the lack of *Thalassia* along the North-to-south study gradient. However, a close examination of the relationship between  $NH_4^+$  concentration and *Thalassia* abundance indicates that in areas of  $NH_4^+$  concentrations greater than 0.015 ppm excludes *Thalassia*. However, in these areas other nutrients except TP are also quite elevated and therefore  $NH_4^+$  alone cannot be implicated.

The Mangrove Transect Comparison showed that the mangrove fringe was a source of total phosphorus and possibly some ammonium to the Bay, but not as much as suspected. The Bay itself was a source of nitrate to the mangrove fringe.  $NH_4^+$  levels in nearshore Biscayne Bay and in the coastal mangrove soils are often quiet high for normal surface waters but probably do not in themselves produce toxicity. One reason for the high concentrations may be groundwater inputs. Anaerobic groundwater contains high levels of  $NH_4^+$  especially the shallow groundwater around the Black Point landfill. High discharge rates of 1-3 l hr<sup>-1</sup> m<sup>-2</sup> (Meeder et al. 1997) may supply a significant and unrecognized N load to the Bay.

## CONCLUSIONS

Freshwaters reaching nearshore Biscayne Bay contains numerous nutrients, metals, hydrocarbons, pesticides, and herbicides from anthropogenic sources. We have quantified nutrients with particular attention to  $NH_4^+$ . Our results indicate a strong correlation between elevated ammonium concentrations with 1) decreased abundance of *Thalassia*, 2) increased abundance of *Halodule* and fast growing algae species, and 3) the increase in filamentous algal cover.

The high salinities encountered during this study are associated with a very dry winter. Therefore, the effects of canal inputs on ambient nutrient concentrations are minimal during this period. The elevated nutrient levels observed should be considered a chronic condition. Conclusions can not be made that ammonia toxicity is solely responsible for the loss of *Thalassia* and other slower growing algae.

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VARIABLE STA **MEDIAN** MIN. MAX. n 10 1.00 12 Surface 0.20 0.02 Salinity 11 12.00 2.20 27.10 12 (psu) 12 11.91 1.40 29.10 12 13 7.80 0.20 26.10 12 14 5.30 37.50 22.40 8 15 26.45 19.20 39.70 12 0.70 23.40 16 5.00 3 17 3.30 3.30 3.30 1 Bottom 10 Salinity 11 20.10 12.40 37.20 11 12 16.40 4.00 33.70 10 (psu) 13 19.90 4.80 36.70 12 14 23.60 11.80 38.00 7 15 26.75 19.30 39.70 12 16 17 Surface 10 25.95 23.30 29.60 12 Temperature 11 25.90 21.40 30.40 12  $(^{\circ}C)$ 12 24.80 23.40 31.60 11 13 25.95 21.90 30.40 12 14 25.45 21.40 30.70 8 31.50 12 15 25.35 20.90 22.05 22.00 22.10 16 2 17 21.70 21.90 2 21.80 Bottom 10 Temperature 29.80 10 11 24.10 20.90  $(^{\circ}C)$ 12 25.05 22.90 28.50 10 13 25.25 23.30 31.20 12 14 30.70 23.80 21.40 7 15 25.35 31.50 12 21.00 16 17 Surface 10 5.70 1.10 8.10 12 4.75 6.80 12 Dissolved 11 1.10 Oxygen 12 3.80 0.40 5.90 11  $(mg l^{-1})$ 13 4.95 1.00 7.30 12 14 5.30 2.70 11.20 8 15 6.90 3.80 8.10 12 16 3.50 1.90 5.10 2 17 3.35 2.30 4.40 2

Table 1. Water quality variable statistics.

VARIABLE	STA	MEDIAN	MIN.	MAX.	п
Bottom	10				
Dissolved	11	5.00	2.10	8.70	10
Oxygen	12	2.50	0.20	6.60	10
$(mg l^{-1})$	13	4.55	1.20	6.80	12
	14	5.70	2.70	11.40	7
	15	7.15	4.80	11.20	12
	16				
	17				
pН	10	7.815	7.397	8.229	11
	11	7.860	7.109	8.370	11
	12	7.800	6.900	8.590	11
	13	7.870	7.100	8.350	11
	14	8.120	7.300	8.463	7
	15	8.370	6.971	8.780	9
	16	7.985	7.500	8.303	4
	17	8.074	7.854	8.500	4
Total	10	4.040	3.141	13.250	12
Organic	11	6.137	3.717	17.010	12
Carbon	12	8.663	4.797	26.358	12
(ppm)	13	6.540	3.813	9.611	12
	14	6.512	4.974	10.102	9
	15	4.990	3.626	7.947	11
	16	11.471	5.274	16.337	4
	17	18.503	6.899	27.450	3
$NO_2^-$	10	0.0070	0.0010	0.0290	12
(ppm)	11	0.0100	0.0020	0.0300	12
	12	0.0280	0.0080	0.1030	12
	13	0.0110	0.0020	0.0320	12
	14	0.0040	0.0020	0.0280	9
	15	0.0100	0.0010	0.0510	12
	16	0.0050	0.0030	0.0350	4
	17	0.0060	0.0040	0.0180	3
$NO_3^{-2}$	10	0.2020	0.0190	0.4120	12
(ppm)	11	0.1090	0.0090	0.4150	12
· · · · ·	12	0.1230	0.0040	0.3870	12
	13	0.1290	0.0140	0.3690	12
	14	0.0950	0.0020	0.1950	9
	15	0.0620	0.0000	0.3380	12
	16	0.0410	0.0340	0.0820	4
	17	0.0300	0.0020	0.0310	3

VARIABLE	STA	MEDIAN	MIN.	MAX.	п
$\mathrm{NH_4}^+$	10	0.0550	0.0170	0.3530	12
(ppm)	11	0.2190	0.0970	0.6720	12
	12	3.2650	0.2220	26.9730	12
	13	0.1760	0.1030	0.7520	12
	14	0.2110	0.0110	0.5150	9
	15	0.0420	0.0040	0.1350	12
	16	0.1130	0.0790	0.4810	4
	17	0.0470	0.0370	0.0480	3
$NH_3$	10	0.00	0.00	0.02	12
(ppb)	11	0.01	0.00	0.04	12
	12	0.11	0.00	0.65	12
	13	0.01	0.00	0.04	12
	14	0.01	0.00	0.03	9
	15	0.00	0.00	0.01	12
	16	0.00	0.00	0.04	4
	17	0.00	0.00	0.00	2
Soluble	10	0.0040	0.0010	0.3060	12
Reactive	11	0.0030	0.0000	0.0280	12
Phosphorus	12	0.0040	0.0010	0.1120	12
(ppm)	13	0.0030	0.0000	0.0190	12
	14	0.0030	0.0000	0.0340	9
	15	0.0020	0.0000	0.1370	12
	16	0.0020	0.0002	0.0620	4
	17	0.0030	0.0004	0.0060	3
Total	10	0.0110	0.0040	0.3230	11
Phosphorus	11	0.0100	0.0030	0.0420	11
(ppm)	12	0.0110	0.0020	0.0300	11
	13	0.0080	0.0020	0.0150	10
	14	0.0080	0.0040	0.0200	8
	15	0.0050	0.0020	0.0170	11
	16	0.0240	0.0060	0.9400	4
	17	0.0120	0.0060	0.0140	3
Total	10	0.2970	0.2060	0.7020	12
Organic	11	0.3910	0.0860	0.6080	12
Nitrogen	12	0.0370	0.0240	0.8570	12
(ppm)	13	0.3180	0.1420	0.5890	12
	14	0.3560	0.1320	1.2040	9
	15	0.3270	0.1790	0.5370	12
	16	0.5660	0.2790	1.4580	4
	17	0.8470	0.3310	1.9860	3

VARIABLE	STA	MEDIAN	MIN.	MAX.	n
Si(OH) <sub>4</sub>	10	1.1840	1.1840	1.1840	2
(ppm)	11	0.6540	0.6540	0.6540	2
	12	0.3370	0.3370	0.3370	2
	13	0.7390	0.7390	0.7390	2
	14				
	15	0.0780	0.0780	0.0780	2
	16				
	17				

Table 2. List of benthic plant taxa.

### BENTHIC PLANT SPECIES

## ANGIOSPERMS

Halodule wrightii Halophila engelmannii Ruppia maritma Syringodium filiforme Thalassia testudinum

#### CHLOROPHYTA

Acetabularia crenulataAnadyomene stellataAvrainvillea nigricansBatophora oerstediaCaulerpa mexicanaCaulerpa racemosaCaulerpa vertcillataHalimeda incrassataHalimeda simulansPenicillus capitatusRhipocephalus phoenixUdotea flabellumUlva lactuca

## РНАЕОРНУТА

Dictyota cf crenulata Rosenvingea sanctae-crusis Sargassum filipendula

## RHODOPHYTA

Acanthophora specifera Chondria littoralis Hypnea cornuta Hypoglossum involvens Laurencia intricata



Figure 1. Map of Black Point Monitoring Program sampling sites in relation to FIU Biscayne Bay water quality monitoring program (+) and South Florida ecosystem.



Figure 2. Locations of Shoreline Ammonia Survey sites in relation to FIU Biscayne Bay water quality monitoring program and major canals.



Figure 3. Map of  $NH_4^+$  concentrations at landfill sites in Oct. 1998.



Figure 4. Map of  $NH_4^+$  concentrations at landfill sites in Nov. 1998.



Figure 5. Map of  $NH_4^+$  concentrations at landfill sites in Dec. 1998.



Figure 6. Map of  $NH_4^+$  concentrations at landfill sites in Jan. 1999.



Figure 7. Map of  $NH_4^+$  concentrations at landfill sites in Mar. 1999.



Figure 8. Map of  $NH_4^+$  concentrations at landfill sites in Apr. 1999.



Figure 9. Map of  $NH_4^+$  concentrations at landfill sites in May 1999.



Figure 10. Map of  $NH_4^+$  concentrations at landfill sites in Jun. 1999.



Figure 11. Map of  $NH_4^+$  concentrations at landfill sites in Aug. 1999.



Figure 12. Map of NH<sub>4</sub><sup>+</sup> concentrations at landfill sites in Sep. 1999.



Figure 13. Map of  $NH_4^+$  concentrations at landfill sites in Oct. 1999.



Figure 14. Map of  $NH_4^+$  concentrations at landfill sites in Dec. 1999.



Figure 15. Box-and-whisker plots of water quality variables by station in the landfill canals.



Figure 16. Box-and-whisker plots of water quality variables by station in the landfill canals.



Figure 17. Comparison of landfill water quality variables from 1994 and current study.



Figure 18. Comparison of landfill water quality variables from 1994 and current study.



Figure 19. Comparison of landfill water quality variables from 1994 and current study.



Figure 20. Comparison of landfill water quality variables from 1994 and current study.



Figure 21. Salinity data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note hypersaline conditions in the south below Military Canal.



Figure 22. Ammonium data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note strong source in and around the Goulds Canal/Black Point area.



Figure 23. Unionized ammonia data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note slightly higher concentrations around the Cutler Canal, Goulds Canal/Black Point area, and Fender Point.



Figure 24. Nitrate data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note strong source from the Cutler Canal.



Figure 25. Total Phosphorus data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note elevated concentrations around Mangrove Key.



Figure 26. Total organic carbon data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note elevated inshore concentrations occurring from Cutler Canal to Mowry Canal.



Figure 27. Total organic nitrogen data from combined Shoreline Ammonia Survey and April 1999 FIU Biscayne Bay water quality monitoring program. Note highest concentrations were found inshore between Goulds and Military Canals.



Figure 28. Plot of NH<sub>4</sub><sup>+</sup> in water and sediments along Shoreline Nutrient Survey sites.



Figure 29. Plot of TP in water and sediments along Shoreline Nutrient Survey sites.



Latitude (N to S)

Figure 30. Plot of plant species distribution along Shoreline Benthic Survey sites.



Figure 31. Plot of *Thalassia* vs salinity along Shoreline Benthic Survey sites.



Figure 32. Plot of *Thalassia* vs  $NH_4^+$  along Shoreline Benthic Survey sites.



Figure 33. Plots of water quality variables from the Mangrove Transect Surveys. Sites are distribution canal (DC) near Military Canal, adjacent mangrove fringe (CF), offshore CF (CBB), mangrove fringe near Mowry (TF), and offshore TF (TBB).