High Time Resolution Monitoring of Inorganic Nitrogen Fluxes into Hillsborough-Tampa Bay from the Alafia River, Florida

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Abstract

Limiting the nutrient loading to the Tampa Bay estuary may improve the growth of seagrasses and the overall quality of the Tampa Bay watershed. As a preliminary step to understanding nutrient loading and recycling within Tampa Bay, we investigated the fluxes of Inorganic Nitrogenous Nutrient (INN) species (ammonium, nitrite, and nitrate) from the Alafia River into the Hillsborough Bay, a segment of the greater Tampa Bay estuary. Sampling was focused on periods of high precipitation during an *El Nino* period, a period when an unusually high precipitation occurred. High concentrations of ammonium were initially seen in surface waters, indicating probable runoff from the nearby Cargill fertilizer plant. With the normal monthly or bi-monthly sampling by this group or the Hillsborough Environmental Protection Commission (HEPC), we found that it was not possible to accurately determine inorganic nitrogen loads, point and non-point sources, or nutrient cycling as a result of the transient character of the inorganic nitrogen fluxes. However, with a High Time Resolution Monitoring (HTRM) program developed by this group, it was possible to identify a region characterized by either vigorous nutrient cycling in which high levels of ammonium were generated locally or as a result of ammonium-rich groundwater discharge, particularly in the more saline bottom waters of the deeper parts of the estuary.

Key Words: Inorganic Nitrogen Nutrient (INN)/ Tampa Bay watershed/ High Time Resolution Monitoring (HEPC)

1. Introduction

High nutrient loads into Tampa Bay have historically had an adverse affect on water quality due to the development of eutrophication. The problem became gradually worse up until the 1980s, primarily as a result of discharge of sewage into the Bay (Martin et al., 1993). Since the early 1980s, however, the eutrophication problem has become less severe due to the introduction of modern tertiary treatment methods for sewage in Hillsborough Bay, but the overall nutrient load continues to be a cause for concern since it appears to be the limiting nutrient in the Bay, phosphate generally being present in excess due to the extensive commercial phosphate operations upstream. One of the principal effects of the high nutrient loads is the increase in the turbidity of the water due to phytoplankton blooms and suspended solids, an effect which is a major obstacle to the long-term seagrass restoration efforts in the Bay (SWIM, Martin et al., 1993). Long-term monitoring by the Hillsborough Environmental Protection Commission (HEPC) indicates that the Alafia River and the portion of Hillsborough Bay into which the Alafia drains has among the highest inorganic nitrogen concentrations anywhere in the Tampa Bay estuary (Figure 1).

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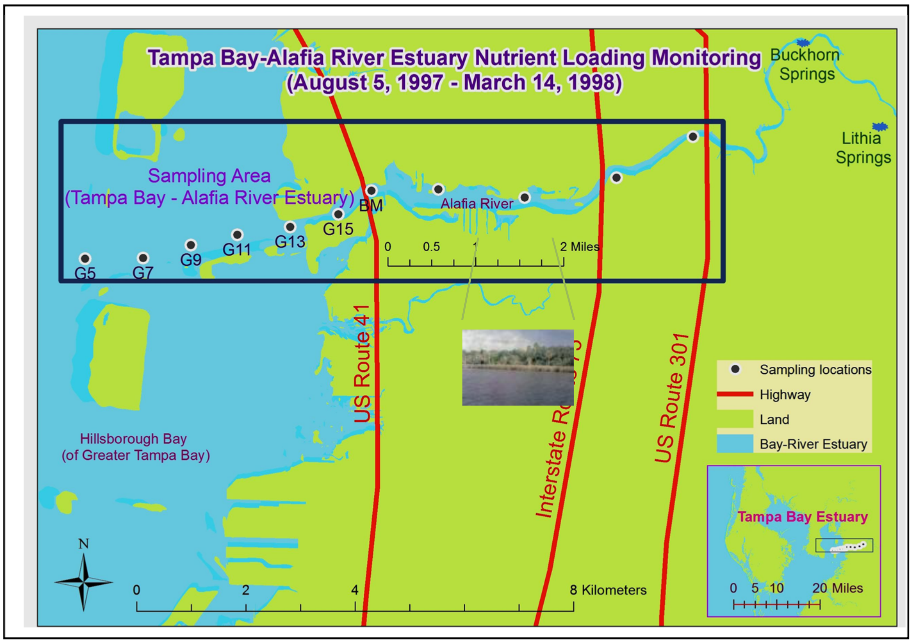


Figure 1 Hillsborough Bay/Alafia River Estuary of Greater Tampa Bay

Since an estimated 22% of the total inorganic nitrogen contribution to Tampa Bay is due to external loading, it is important to be aware of both long-term changes in the external nutrient loads and transient variability in the loads. Monitoring by the Hillsborough EPC appears to be inadequate to document important variability in nutrient fluxes. Moreover, high time resolution spatial sampling may be useful in identifying point sources, especially before and after high precipitation events (or storm events). Routine bi-monthly monitoring by Hillsborough EPC was thought insufficient to identify point sources. Some of these point sources were the subject of investigations at the time by South West Florida Water Management District or SWFMD (e.g. Lithia and Buckhorn Springs in the upper reaches of the Alafia River, Jones et al., 1996, See Figure 1). Initially, the Cargill fertilizer plant located approximately 1.3 – 1.6 km (0.8 – 1.0 mile) upstream of the mouth of the Alafia River was thought to be a potential source of nutrients, especially ammonium. Non-point sources of nitrogen include fertilizers from agricultural and urban runoff, animal manure, and atmospheric deposition. Inorganic nitrogen released from the degradation of accumulated organic matter in the bay sediments, however, has not been directly measured and can be a significant non-point source contributor to the overall nutrient loading in the bay (Martin et al., 1993). In general, storm-water is responsible for delivering most of the nutrients from the point and non-point sources during the mid and late summer, a period typically accounting for the bulk of the storm runoff during the year. However, during the winter of 1997-1998, high rainfall due to *El Nino* conditions (Table 1) effectively extended the season in which storm runoff was an important source of inorganic nitrogen loading.

2. Objectives

The objectives of this research project was to identify point and non-point sources of inorganic nitrogenous nutrients (especially ammonium and nitrate), and determine effects of precipitation events on inorganic nutrient loadings within the Tampa Bay – Alafia River Estuary. Thus, the objective of the research is to determine the temporal variability and spatial distribution of inorganic nitrogenous nutrients within the estuary with a focus on monitoring before and after storm events. With data from monitoring, especially the (HTRM) program, chemographs of nitrate, ammonium, dissolved oxygen (DO) were developed and correlated with hydrograph data from the United States Geological Station (USGS) river-discharge station at Lithia.

3. Materials & Method

Measurements of temperature, salinity, pH and dissolved oxygen (DO) were carried out using commercially available field instruments. Concentrations of ammonium and nitrate-nitrite (combined), together termed "Inorganic Nitrogenous Nutrients (INN)", were performed by collecting water samples along a predetermined sampling transect. Subsequently, colorimetric and ion chromatographic (IC) analysis were done to determine INN values, following the analytical protocol given in "*Methods of Sea Water Analysis*" by Grasshoff, 1988. Probe leads & sampling devices, including Tygon™ water draw tube, were designed to reach a depth of at least 4 meters (m) from the water surface. Surface and subsurface samples were collected into a Bottle Top Filter Holder (vacuum-type by Nalge) and passed immediately through 0.45 µm filters. The filtered samples were stored in ice and analyzed within a few hours of sampling. A pontoon type boat was used to travel to sampling sites. Geographical Information Systems (GIS) maps were prepared using ArcGIS 9.1 and ArcGIS 10 software (Redlands, California, USA) with Spatial Analyst Tool and the Geostatistical Tool. Inverse Distance Weighting (IDW) was used for the spatial analysis and geostatistical work to develop the time-series maps (Davis, 2002). Since comparison of trends and variations in graphs (e.g. DO vs. ammonium) involved large differences from approximately a factor of two to as much as several orders of magnitude, it was not thought necessary to include error bars or other types of statistical analysis in the graphs developed, because all sampling and analysis confirmed a total error of less than 10% of the analytical value obtained. This error is insignificant when compared with the differences in trends or values of interest (Harris, 1996).

Table 1 Comparison of Historical (monthly) &*El Nino* precipitation levels in the Tampa Bay area.

Month	Historical*	1997**	1998**
January	1.99	0.95	**4.64**
February	3.08	0.66	**10.82**
March	3.01	1.28	**5.16**
April	1.15	10.71	0.41
May	3.1	1.7	1.96
June	5.48	1.46	2.65
July	6.58	6.73	12.95
August	7.61	8.2	6.55
September	5.98	**12.84**	8.42
October	2.02	**4.2**	0.47
November	1.77	**3.41**	0.4
December	2.15	**15.57**	0.92

* Source: Southeast Regional Climate Center. ** National Weather Service, Tampa, Florida.

*** Area highlighted in gray represents period of abnormally high precipitation due to *El Nino*.

4. Study Location

As a preliminary step to understanding the complex nutrient loading and recycling mechanism within the Tampa Bay watershed, sampling for analysis of nitrate (and nitrite combined), ammonium, silicate and phosphate was carried out along a transect starting from a point in Hillsborough Bay (mean depth 3.3 m) located 3.2 km (~ two miles) from the mouth of the Alafia River and then extending 12.5 km (7.8 miles) up into the Alafia River. Over this transect, between 5 – 17 samples were collected at 0.8 to 1.6 km (0.5 – 1.0 mile) intervals (Figure 2 and Table 2). At each location pH, salinity, and dissolved oxygen (DO) were measured and a (filtered) water sample was collected for nutrient analysis. Due to the lack of a significant correlation between silica and phosphate, or between these nutrients and the other nutrients (ammonium & nitrate), the analysis for silicate and phosphate was discontinued after about two months of monitoring. Also, at each location water samples were collected at the surface (depth 0-0.5 m), and during the latter sampling stages (on 11/2/1997 or Nov. 2, 1997 and onwards), at a depth of 1.0 – 2.5 meters.

Table 2 Locations of sampling points in Hillsborough Bay and the Alafia River

Sampling Site	Location	Approximate distance from zero-mile reference
GM-3	In Hillsborough Bay (Green-Channel Marker 3)	**0 miles** (“zero-mile” *Reference point*)
GM-5	In Hillsborough Bay (Green-Channel Marker 5)	0.5 miles (0.8 km)
GM-7	In Hillsborough Bay (Green-Channel Marker 7).	1.0 miles (1.6 km)
GM-9	In Hillsborough Bay (Green-Channel Marker 9).	1.5 miles (2.4 km)
GM-11	In Hillsborough Bay (Green-Channel Marker 11) and about 1/8 of a mile from the mouth of the Alafia river.	2.0 miles (3.2 km)
GM-13	In the Alafia river (Green-Channel Marker 13).	2.5 miles (4.0 km)
GM-15	In the Alafia river (Green-Channel Marker 15) and within a few meters of the Cargill fertilizer plant (depth approx. 3-10 m).	3.0 miles (4.8 km)
BM	Boat Marina, located on the Alafia River (depth approx. 3-4 m).	3.6 miles (5.8 km)

All the mentioned (above) sampling points have been marked with respect to distance from the defined zero-mile reference Green-Channel Marker 3 or GM-3. The depth of relatively deep points, i.e. GM-15 and BM, are given within brackets in the Location-column.

5. Initial Study

The initial monitoring began on August 5th 1997, a period normally having a high intensity of thunderstorms, and continued at 1 -3 week intervals until November 22nd 1997, sampling 2-3 times a month (Table 2 for monthly rainfall information). This sampling program was categorized later as the Background Sampling Program (BSP). Most of the data was gathered during and after periods of high precipitation (storm events). Initial data from these sampling locations reveal the possibility of a significant point source of ammonium located approximately 1.6 km (1 mile) upstream of the river/bay interface, near sampling location (GM-15).

6. Detailed Study

Based on the initial study, it was suspected that the location near Cargill Fertilizer Plant (location GM-15) was a point source of ammonium. However, some of the sampling days showed bottom waters of the deeper part of the estuary were significantly higher in ammonium than that of the less saline surface waters at the same location, particularly after storm events. To further investigate these high-levels of ammonium, especially at location GM-15, sampling rates were intensified so as to reach 4-5 sampling days per month. To meet this goal, an intense sampling program between Dec. 6, 1997 and Feb. 20, 1998 consisting of nine sampling days was carried out, referred to here as the Intensive Sampling Program (ISP) In addition, a High Time Resolution Monitoring Program (HTRM) covering an isolated storm event (on the night of March 7, 1997) consisting of seven days of sampling between March 6, 1998 – March 14, was done. Chemographs (e.g. DO vs. ammonium) were developed for each of the sampling programs.

7. Results & Discussion

During the BSP, concentrations of ammonium ranged from 0.0 – 1.2 mg/L (0.0 – 68.8 µM) for the less saline surface waters, and 0 – 3.3 mg/L (0.0 - 18.3 µM) for the more saline deeper waters. Concentrations of nitrate during the BSP ranged from 0 – 1.5 mg/L (0.4 to 82.7 µM) for surface waters, and 0.1 – 1.0 (2.9 - 56.3 µM) for the deeper waters. For the ISP, ammonium concentration of the surface waters ranged from 0.0 – 4.6 mg/L (2.5 - 255.6 µM), while the deeper waters showed values ranging from 0.0 – 2.5 mg/L (0.0 - 136.8 µM). Nitrate concentrations for the ISP ranged from 0.2 – 3.4 mg/L (11.3 - 190.3 µM) for surface waters while the range for the deeper waters ranged from 0.1 – 1.9 mg/L (4.0 – 105.4 µM). Most of the high nitrate concentrations were seen as originating from fresh river water upstream, highly likely from Lithia & Buckhorn Springs (Figure 1), while most of the high ammonium concentrations were found near sampling location GM-15 (close to the Cargill Fertilizer plant), with the highest values found in deep rather than shallow water. Overall the concentrations of ammonium were normally similar in magnitude to the nitrate concentrations for both surface and deeper water, but showed distinctly higher levels than the nitrate during certain sampling days, especially during the ISP. It was also noted that that ammonium concentrations reached very high levels a few days after storm events, particularly near sampling location GM-15, a part of the estuary that is relatively deep (Figure 1).

During the ISP it was also noticed that five days prior to an increase in ammonium concentration for GM-15 that took place at depth on January 31, 1998 a decrease in DO occurred (January 26, 1998) generally in the deeper waters (Figure 2) This depressed DO concentration in the deeper waters then coexisted with the elevated ammonium levels on Jan. 31, 1998. Thus this increase in ammonium appears at a time when the river flow rate decreases substantially, i.e. about 4 – 6 days after a period of high precipitation (hydrograph of Figure 2). This can be observed from the hydrograph, which peaks around Jan. 26 (flow/discharge rate 37 cu. m/sec) before decreasing substantially to 18 m^3/sec on Jan. 31.

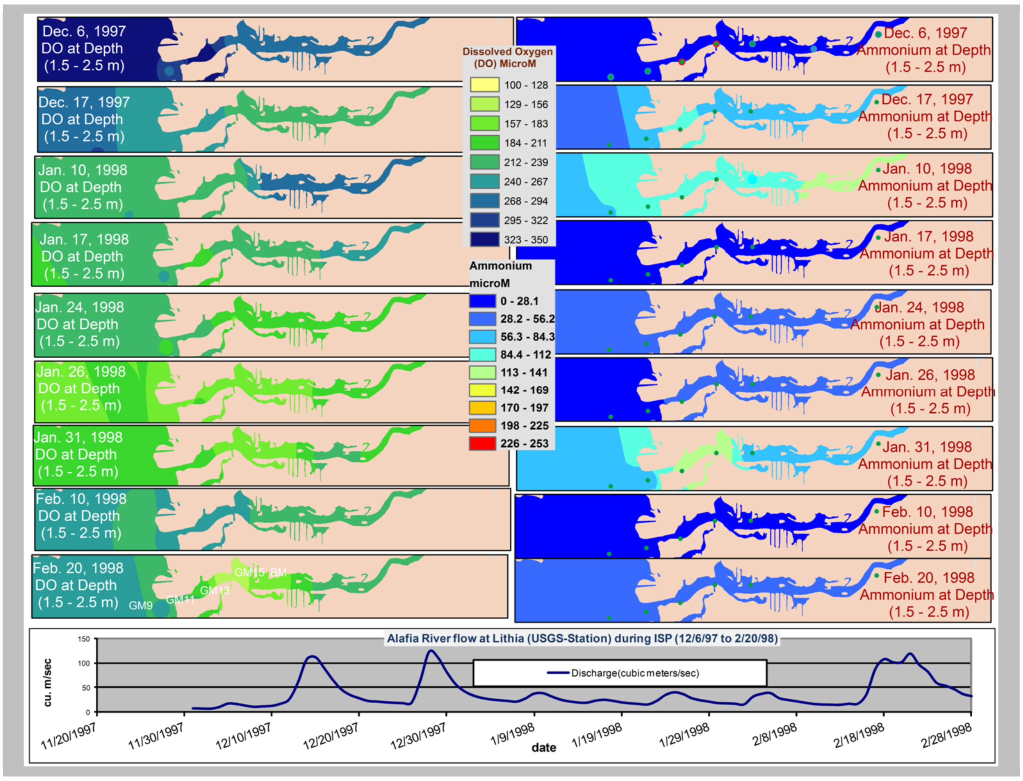


Figure 2 Mapping of Ammonium (*right*) at depth, 1 – 300 µM (0 – 5.4 mg/l) and DO (*left*) at depth, 1 – 450 µM (range 0.0 – 14.4 mg/l) concentrations and River Discharge hydrograph (below) in m^3/sec at Lithia, (December 6, 1997 – February 20, 1998)

Since it appeared from the ISP that storm events had an effect on elevated ammonium concentrations in the deeper parts of the estuary, particularly at sampling location GM-15, determining the origins of these high ammonium concentrations in the deep locations (e.g. GM-15) became an objective of the High Time Resolution Monitoring HTRM program. For example, sampling was carried out on seven days between March 6 & 14, 1998. Since the salinity of the bottom waters (1.5 – 2.5 m) differed from that of the surface waters (0 – 0.5 m), it was also thought necessary to determine if the more saline Hillsborough Bay waters were bringing the high concentrations of ammonium into this area via tidal-fluxes to the deeper parts of the Alafia river estuary, or whether there is another source for these large concentrations of ammonium.

Like the ISP, the HTRM also showed evidence that the deeper parts of the estuary, e.g. GM-15 and BM, were possible point sources of ammonium (Figure 3). Additionally, it can be seen by comparing salinity values with ammonium concentrations at the Alafia River estuary on March 12, 13 & 14 (Figure 3 & Figure 4 (e)), that the tidal fluxes inferred from salinity values have little or no bearing on the high ammonium concentrations observed in the relatively deeper parts of the estuary (i.e. GM-15 and BM). From the salinity of the deeper waters, it appears that the tide is coming in on March 12 and 13, while moving away from the estuary on March 14, which strongly suggests that tidal activity cannot explain the high concentrations throughout this period.

From the discussion above, it can be inferred that there may be a point source for ammonium at sampling locations GM-15 and BM, most likely at depth. Since these sampling locations are separated by 0.8 km, there appear to be two separate point sources involved. Also, as was observed on Feb. 26 and Feb. 31 (Figure 2), a noticeable reduction in DO is observed first on March 12, 1998 before an increase in ammonium occurs on March 13 and 14, 1998 (Figure 3). These increases in ammonium, particularly at depth, are seen 7 and 8 days after a storm event ("hydrograph" of Figure 4 (a)). For the entire HTRM the surface ammonium concentrations ranged from 0.0 – 3.0 milligrams/liter or mg/L (0.0 - 164.8 μM) (Figure 4 (b)) for all the sampling points, while the depth concentrations ranged from 0 – 4.6 mg/L (0.0 - 253.3 μM) (Figure 4 (C)), with the maximum concentrations occurring at depth in the vicinity of GM-15 and BM (Figure 4 (a)).

The early part of the HTRM (e.g. March 8, 9, and 10, 1998) showed relatively higher values for DO in surface waters as compared to those found at depth during the late HTRM (i.e. March 12, 13 and 14, map in Figure 3). The surface DO concentrations averaged 8.1 mg/L (253.9 μM), 7.3 mg/L (228.8 μM) and 7.8 mg/l (243.9 μM) for the sampling days March 8, 9 and 10, 1998, respectively, for the entire sampling transect. For these same days, i.e. March 8, 9, and 10, 1998, the DO concentrations at depth averaged 8.1 mg/l (252.2 μM), 7.4 mg/L (229.7 μM) and 6.5 mg/l (202.8 μM), map in Figure 3 *&* Figure 4(d).

The late HTRM surface DO concentrations for March 12, 13 and 14, 1998 averaged 6.5 mg/L (208.1 μM), 7.5 mg/L (233.6 μM) and 7.2 mg/L (225.6 μM), respectively over the entire transect, while the DO at depth for the same days averaged 5.4 mg/L (168.4 μM), 5.5 mg/L (171.6 μM) and 6.9 mg/L (214.4 μM) respectively. The concentrations of DO at depth for March 12, 13 and 14, 1998 at the relatively deep location, GM-15, were 4.0 mg/L (125.6 μM), 4.1 mg/L (126.6 μM) and 5.3 mg/L (164.4 μM), respectively (Table 3), while the DO concentrations for BM at depth for these same days (March 12, 13 and 14) were, 3.6 mg/L (112.8 μM), 5.2 mg/L (162.5 μM) and 4.8 mg/L (150.0 μM), respectively, while surface waters at these same locations, i.e. GM-15 and BM, had significantly higher DO for these same days (March 12, 13 and 14), 6.7 mg/L (210.6 μM), 7.2 mg/L (225.0 μM) and 6.2 mg/L (193.8 μM) for surface GM-15, and 7.2 mg/L (224.1 μM), 7.4 mg/L (231.6 μM) and 6.7 mg/L (209.2 μM) for surface BM, respectively.

It is also interesting to note that low DO concentrations are seen on March 6th, at depth, especially for GM-15 and BM, where the concentrations were 4.1 mg/L (129.1 μM) and 4.3 mg/L (135.9 μM), while in contrast the average surface concentration of DO was 8.6 mg/L (269.5 μM) with a lowest value of 7.3 mg/L (228.1 μM) for the transect sampled on that day (i.e. March 6). This day, March 6 (river discharge–30 m^3/sec) was a few days after a storm event, which gave a peak discharge of 48 m^3/sec on March 3, 1998.

Additionally it was interesting to note that the ORP (mV) for the latter part of the HTRM, i.e., March 12, 13 and 14, was much higher for the entire transect, especially at depth when compared with the entire sampling transect of the surface and depth water of the early part of the HTRM, e.g. March 6, 8, 9 and 10, 1998 (Table 4) or for the range for surface waters of the entire transect of the late HTRM (i.e. March 12, 13 and 14). For example, the range for the average deep ORP samples for March 12, 13 and 14 (i.e. late HTRM), is 197.3 to 225.5 mV, which is much higher than the range for the average surface ORP (-1.4 to 94.5 mV) for the same period, and even higher than the range obtained for the entire transect for surface and depth for the early part of the HTRM (March 6, 8 , 9 and 10, -39.3 to 2.6 mV in the surface samples and -27.5 – 24.0 mV in the samples collected at depth).

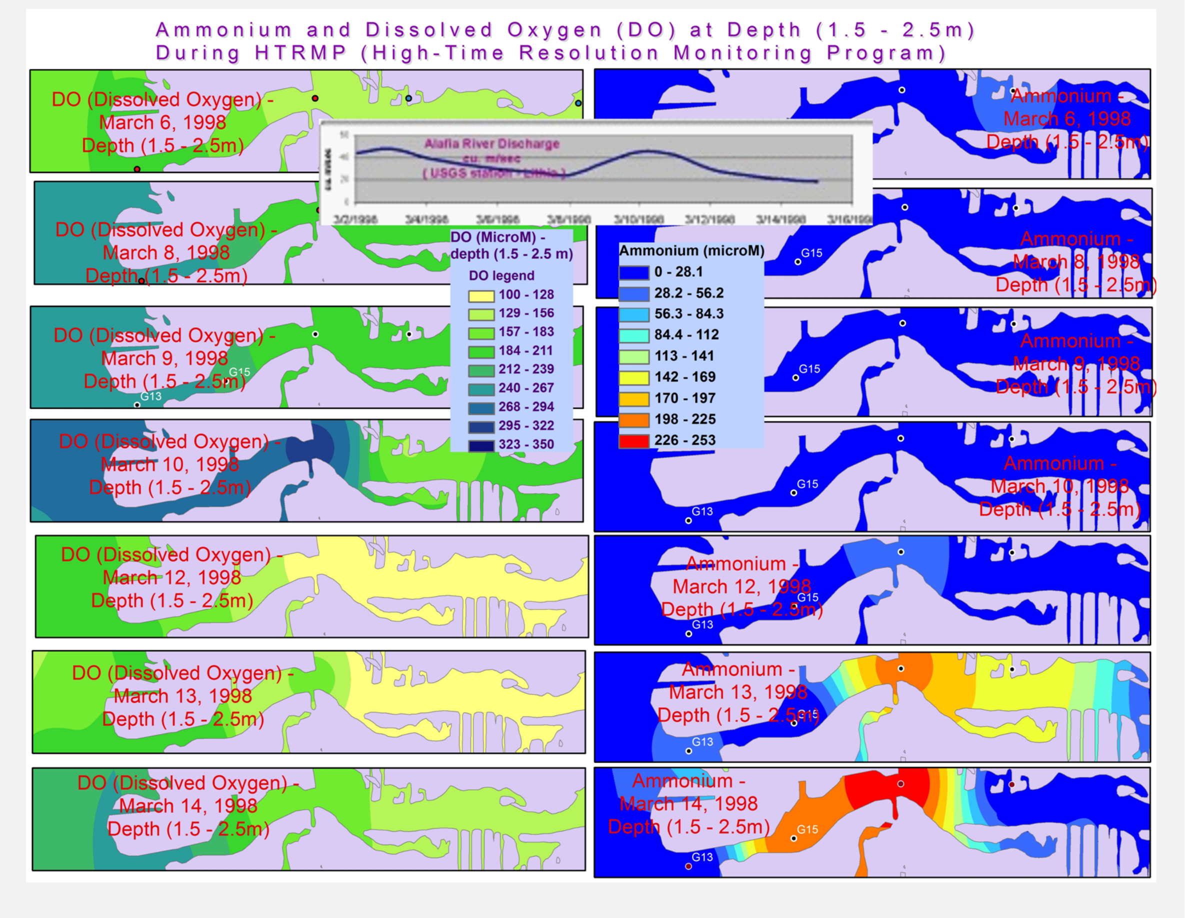
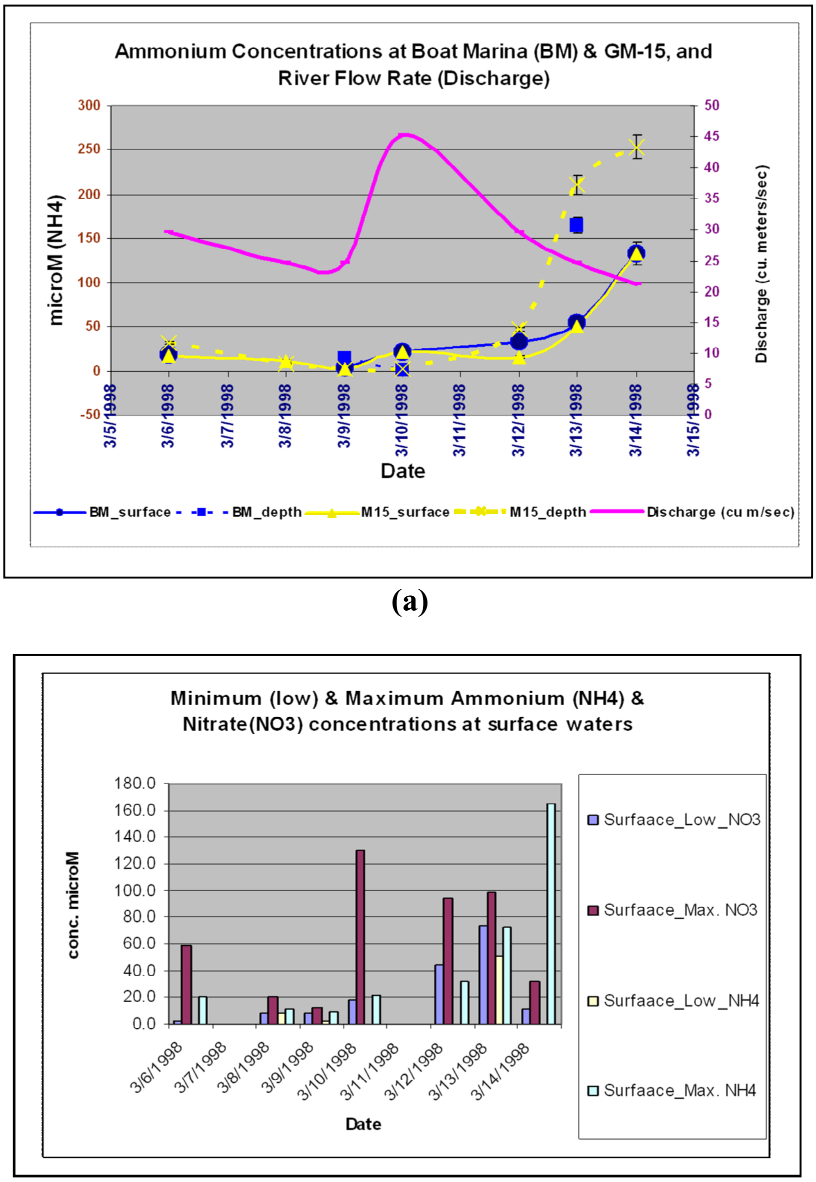


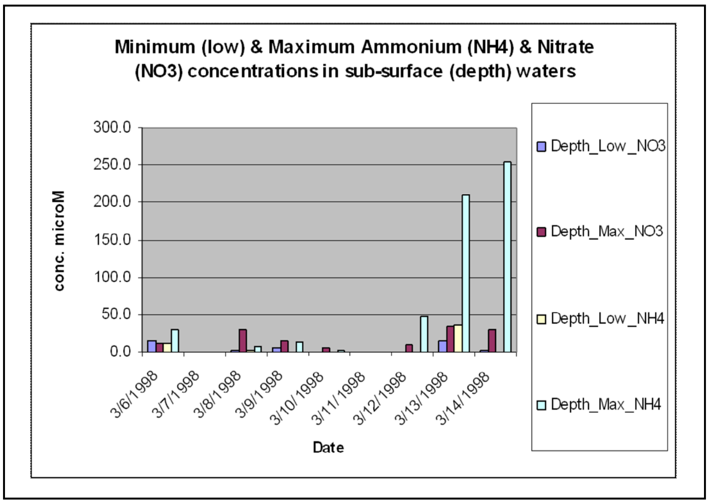
Figure 3 DO (3.2 – 9.6 mg/l or 100 – 350 µM) and Ammonium (0 – 4.6 mg/l or 0 – 253 µM) Concentrations of HTRM Program (March 6 – 14, 1998), *Note* the storm event on the night of March 7, 1998 causing a peak in river-flow on March 10, 1998 (or day 5 of HTRM). The above time series was developed using Inverse Distance Weighting (IDW) method (Spatial Analyst Tool of ArcGIS 10).



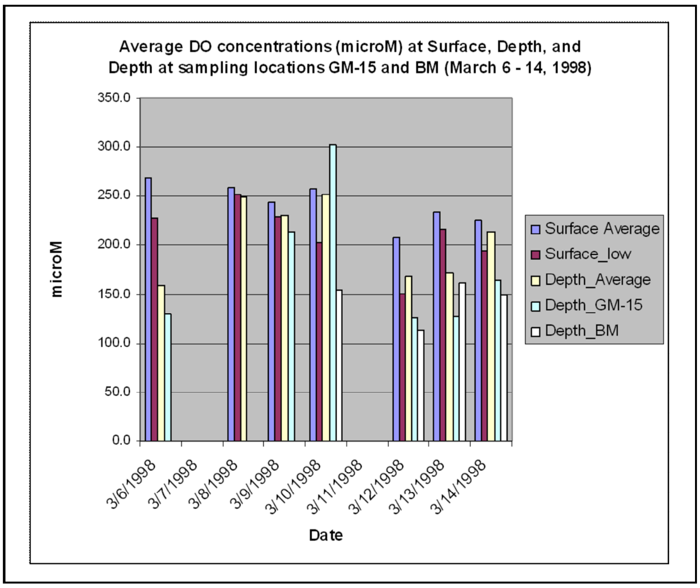
(a)

(b)

Figure 4 (a) River Discharge hydrograph in m^3/sec, and ammonium concentrations at sampling locations GM – 15 & BM at surface and depth. (**b**) Minimum and maximum ammonium and nitrate concentrations in surface waters for all points on the transect for each sampling day of HTRM (i.e. March 6, 8, 9, 10, 12, 13 and 14, 1998)

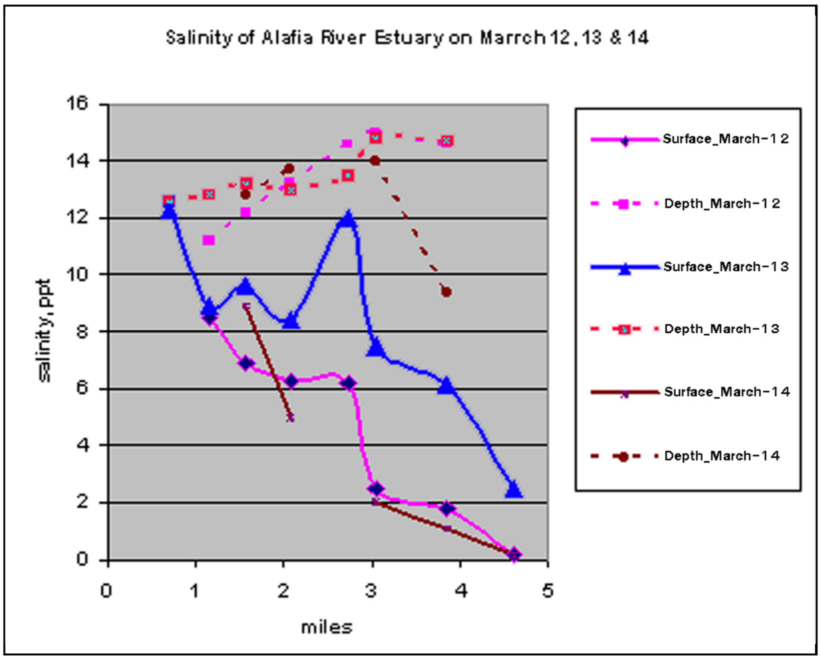


(c)



(d)

Figure 4 (c) Ammonium concentrations at sampling locations GM – 15 & BM, and minimum and maximum ammonium and nitrate concentrations at depth for all points on the transect for each sampling day of HTRM (i.e. March 6, 8, 9, 10, 12, 13 and 14, 1998) and **(d)**, Average DO at surface and depth (1.5 – 2.5 m), and concentrations of DO at GM-15 and BM during HTRM.



(e)

Figure 4 (e) Salinity in ppt (parts-per thousand) of the Alafia River Estuary on March 12, 13 & 14 of HTRM at both the surface and at depth.

Table 3 Concentration of surface (left) and depth for DO at GM-15, BM and the average for all other locations (excluding GM-15 & BM).

Sampling Day	**DO conc. at surface in mg/L (µM)**			**DO conc. at depth in mg/L (µM)**		
	GM-15	**BM**	**Average for all other locations**	**GM-15**	**BM**	**Average for all other locations**
6-Mar	**7.1** (228.1)	**7.1** (228.1)	**9.3** (290.2)	**4.1** (129.1)	**4.3** (135.9)	**5.5** (172.5)
8-Mar	**8.1** (252.2)	-	**8.4** (263.1)	-	-	**8.0** (249.5)
9-Mar	**7.4** (229.7)	**8.0** (250.3)	**7.9** (247.1)	**6.9** (214.1)	**6.9** (214.4)	**7.7** (241.0)
10-Mar	**8.2** (254.7)	**6.5** (202.8)	**8.7** (272.7)	**9.7** (303.1)	**4.9** (154.1)	**8.8** (275.0)
12-Mar	**6.3** (210.6)	**7.2** (224.1)	**6.5** (204.6)	**4.0** (125.6)	**3.6** (112.8)	**6.2** (193.0)
13-Mar	**7.2** (225.0)	**7.4** (231.6)	**7.6** (237.1)	**4.1** (126.6)	**5.2** (162.5)	**6.4** (198.6)
14-Mar	**6.2** (193.8)	**6.7** (209.2)	**7.5** (233.7)	**5.3** (164.7)	**4.8** (150.0)	**7.6** (237.1)

Moreover, very low pH values ranging from 3.3 to 3.9 are observed at depth for the entire transect for the later part of the HTRM (March 12-14), particularly when compared with average transect surface and depth pH ranges for the early part of the HTRM (7.2 to 7.9 in the surface samples and 6.8 to 7.7 in the samples collected at depth, Table 4).

Table 4 Average and range of ORP (Oxy-Reduction Potential in mV) and pH for surface and deep waters during the HTRM for the entire sampling transect.

Sampling Day (March 6 - 14, 1998)	mV (ORP or Oxy-Reduction Potential)				pH			
	Surface Average	Surface Range	Depth Average	Depth Range	Surface Average	Surface Range	Depth Average	Depth Range
6-Mar	-39.3	-90 to -13	-27.5	-52 to -3	7.9	7.4 - 8.7	7.7	7.3 - 8.1
8-Mar	0.7	19 to -39	24.0	23 to 25	7.5	6.9 - 7.9	6.8	6.7 - 6.8
9-Mar	2.6	-22 to 31	21.8	5 to 59	7.2	6.7 - 7.6	7.1	6.3 - 7.9
10-Mar	-34.7	-59 to -7	-13.6	-55 to 72	7.8	7.3 - 8.1	7.5	6.2 - 8.2
12-Mar	-1.4	-13 to 15	215.8	172 to 252	7.1	6.8 - 7.3	3.9	3.5 - 4.3
13-Mar	-7	-3 to -15	197.3	184 - 226	7.4	7.2 - 7.5	3.9	3.5 - 4.3
14-Mar	94.5	27 - 143	225.5	212 to 247	5.5	4.7 - 6.7	3.3	2.9 - 3.6

8. Discussion

The HTRM was able to identify at least two possible point sources originating in the deeper zones of the estuary at GM-15 and BM. The HTRM also revealed that the Cargill fertilizer plant (sampling location GM-15) may not be a source of ammonium to the estuary, since surface waters near the plant do not show elevated ammonium concentrations after storm events.

Four possible explanations for the high concentrations of ammonium at these two locations are considered:

1. Groundwater rich in ammonium may have been discharging at these two locations after periods of high precipitation. The surface water within the drainage basin of the Alafia River could accumulate ammonium from agriculture existing and forest-runoff and this may have been transported into deeper groundwater zones. Due to the highly porous karst-system existing in South Florida, the ammonium-rich groundwater could discharge into the estuary within a few days after a storm event.
    a) Vigorous nutrient cycling in the benthos or riverbed at these two locations is another possible explanation. As seen in Equation (1), ammonium is released as a result of the oxidation of organic matter (Buffle and De Vitre, 1994). Large quantities of organic matter could be accumulating at these deeper locations, which then release ammonium to the bottom waters. The drop in DO seen at the bottom water of these locations after storm events could be explained in the same way, with oxygen consumed in the degradation of organic matter. However, if this is the case, an immediate release of ammonium coincident with the drop in DO would be expected, rather than a delayed release of ammonium as observed even though there is a possibility of the release of ammonium being delayed due to ammonium having to make its way into the overlying water from the bulk of the decaying organic matter in the benthos. As the equation below suggests initially dissolved oxygen may act as the electron acceptor, but with the depletion of DO, sulfate (SO_4^{2-}), abundant in estuarine highly saline bottom waters could act a major electron acceptor of the oxidizing organic matter (Canfield et al., 2005).

$$\text{ORGANIC MATTER}+\text{OXYDANTS }(O_2, SO_4^{2-},..) \longrightarrow 106\ CO_2+16\ NH_4^+ + HPO_4^{2-} + HS^- + \text{Trace Elements} \quad (1)$$

b) Ammonium rich particulate could be washed from the vicinity of these two locations into the estuary, then settling in the bottom waters. This explanation, however, requires that little ammonium-rich particulate dissolves in the surface waters, since these do not show the same increase in ammonium. It also does not clearly explain the delay between storm events and the increase in ammonium.

c) The increase in ammonium originating from a deep source (either local organic matter oxidation or groundwater flow) could be due to the decrease in dilution as the river stage drops after a storm. This hypothesis could be fully tested if more samples were available from periods between storms, since a dilution effect would show up as a decrease in ammonium and increase in DO during storms that then gradually relax back to "normal" values for deep samples as the effect of the storm disappears. At present, there is insufficient data to fully evaluate this explanation.

Given the available data, we cannot demonstrate unequivocally that one of the explanations offered above is correct. A local source of ammonium resulting from organic matter degradation does not appear likely because this process is more likely to contribute to a non-point source. In addition, it appears unlikely that organic matter degradation could respond so quickly, on the time scale of just days. Washing of particulate ammonium seems a possible explanation only if the dissolution of the ammonium particulates was slower than the setting velocity. An increase in ammonium-rich groundwater several days after the storm event seems quite possible, but to distinguish this from Explanation 4 would require additional data on ammonium concentrations between storm events.

The high concentration of nitrate during the HTRM was probably due to the large quantities of nitrate entering the Alafia from Lithia and Buckhorn springs, and or due to the oxidation of ammonium to first nitrite (see Equation (2) below) by *Nitrosomanas europea*, a lithotrophic chemotroph nitrifying bacteria, and then the subsequent oxidation of nitrite to nitrate (Buffle and De Vitre, 1994).

$$2\ NH^+_4 + 3\ O_{2\,(aq)} \longrightarrow 2\ NO^-_2 + 2\ H_2O + 2\ H^+ \qquad (2)$$

The low pH could be accounted by the above equation. Additionally the low pH could also be accounted by the following Equation (3) (Appelo et al., 2009, Snoeyink et al., 1980 and Millero, 2006) where HS^- ions (hydrosulfide) in Equation 1 get oxidized by DO to SO_4^{2-} producing H^+ ions mediated by microbes such as *Thiobacillus* (Madigan et al., 2006) or in general the more common Equation (4) (Canfield et al., 2005) or similar microbial mediated reactions.

$$2\ HS^-_{(aq)} + 4\ O_{2\,(aq)} \longrightarrow 2\ SO_4^{2-} + 2\ H^+ \qquad (3)$$

$$H_2S_{\,(aq)} + 2O_{2\,(aq)} \longrightarrow H_2SO_4 \qquad (4)$$

9. Conclusions

The HTRM revealed that temporal and spatial monitoring are important when trying to determine inorganic nitrogen loads. The program was successful in providing evidence of a likely deep water or sediment source for high ammonium concentrations. With more high time resolution monitoring (including monitoring additional higher salinity bottom waters), data from this and other parts of the estuary (Alafia & Tampa Bay) can be collected, thus providing a better understanding of the relationship between river discharge and precipitation. This would make it possible to average data over a longer period of time and to improve estimates of nutrient loadings into Tampa Bay.

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