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Spatial and Temporal Chemical Variations in the Hillsborough River System

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Spatial and Temporal Chemical Variations in the Hillsborough River System

by

Lori A. Pillsbury

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
College of Marine Science
University of South Florida

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Spatial and Temporal Chemical Variations in the Hillsborough River System

Lori A. Pillsbury

ABSTRACT

The Hillsborough River flows southwesterly through Pasco and Hillsborough counties in west central Florida. From its source at the Green Swamp to its mouth in Hillsborough Bay, the river is joined by many tributaries and man-made inputs. Spatial and temporal variations in the river's major ion and CO₂ system chemistry were examined in a two-year study between 1999 and 2001. At thirteen sampling stations along approximately 54 miles of the river, water samples were collected in surroundings that ranged from pristine to urban. Samples were collected monthly for the first year and periodically thereafter. Concentrations of major ions were lowest in the river's headwaters, showed only minor spatial variations in mid-river, and sharply increased in tidally influenced waters below a dam on the lower river. A major tributary, Blackwater Creek, exerts a strong influence on the river's phosphate concentrations, and Crystal Springs, upstream of Blackwater Creek, exerts a strong influence on nitrate concentrations in the river. Downstream of Crystal springs, NO₃⁻ concentrations decreased steadily to levels that are more than an order of magnitude lower than levels in the upper river. Temporal ion concentration variations can be quite large. Low major ion concentrations were observed in the rainy season (June –

September), while phosphate concentrations increased dramatically during extremely wet conditions. Seasonal variations were also observed in the river's CO₂ system. Riverwater pH decreased during periods of high precipitation along with CaCO₃ saturation state. CaCO₃ supersaturation was observed during the exceptionally dry periods of the study, and undersaturation was observed during periods of high rainfall. Overall, the chemistry of the Hillsborough River is greatly influenced by temporal and spatial variations in the river's tributaries, groundwater sources, and anthropogenic inputs.

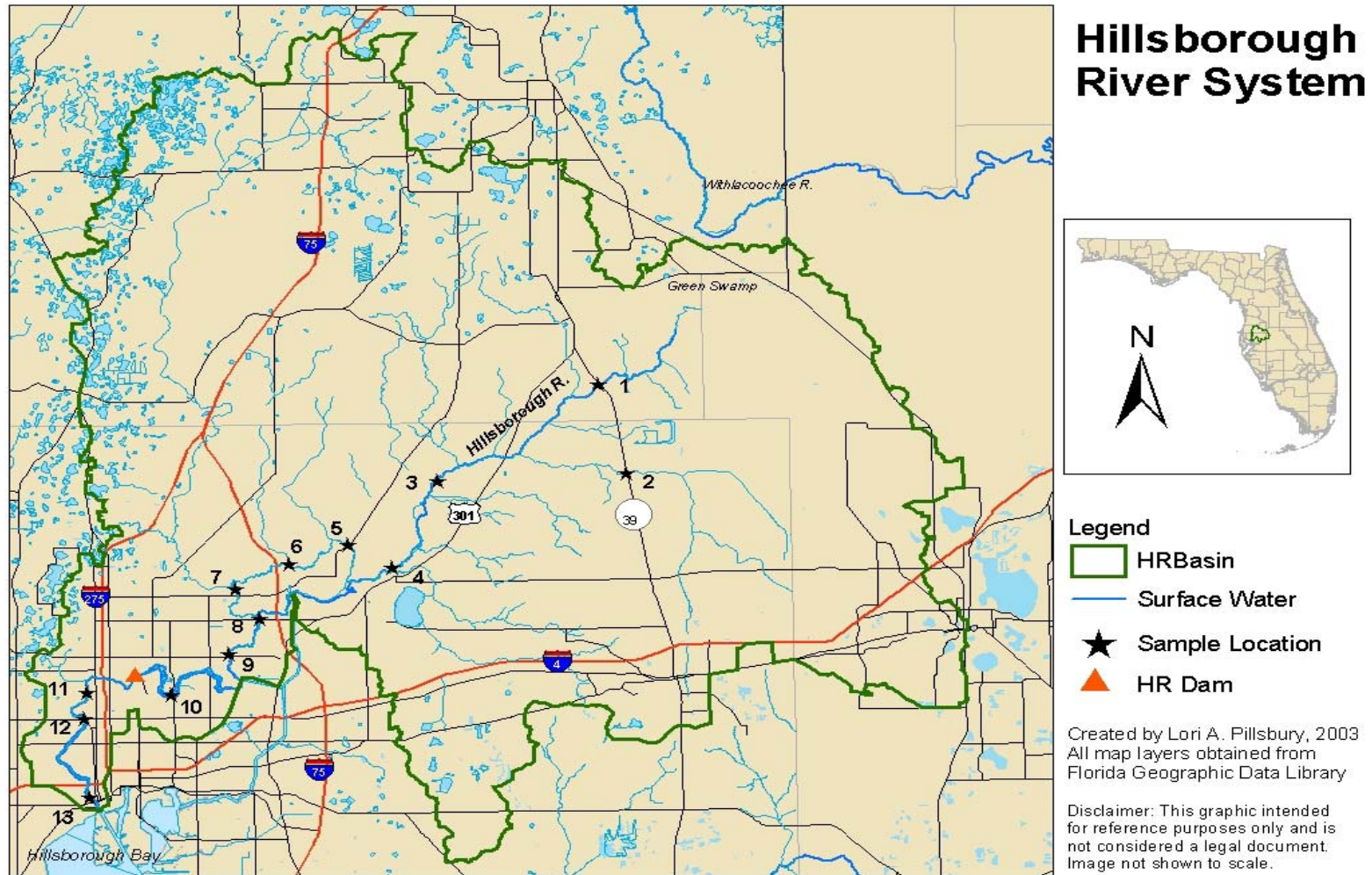
Introduction

The Hillsborough River flows approximately 54 miles from its source in the Green Swamp to its mouth at Hillsborough Bay (Figure 1). Used for over 10,000 years by Timucuan, Calusa, and Seminole Indians, the river was originally called the Lockcha-popka-chiska, meaning “river where one crosses to eat acorns” (Florida Department of Natural Resources, 1989). The river was renamed by the British presumably after the Earl of Hillsborough. Along the banks of the river, there are many historical and archaeological sites. These include Native American burial mounds, Fort Foster (built during the Seminole wars), and several historic buildings along the lower river.

As the river flows toward Hillsborough Bay, water is added from several tributaries and springs, Figure 2. Crystal Springs is the major source of freshwater for the river. Once a recreation area open to the public, Crystal Springs is now the major source of water for the Zephyrhills Spring Water bottling facility. South of Crystal Springs lies a unique tributary of the Hillsborough River, Blackwater Creek. Blackwater Creek drains a large agricultural and phosphate processing area and adds nutrients to the river.

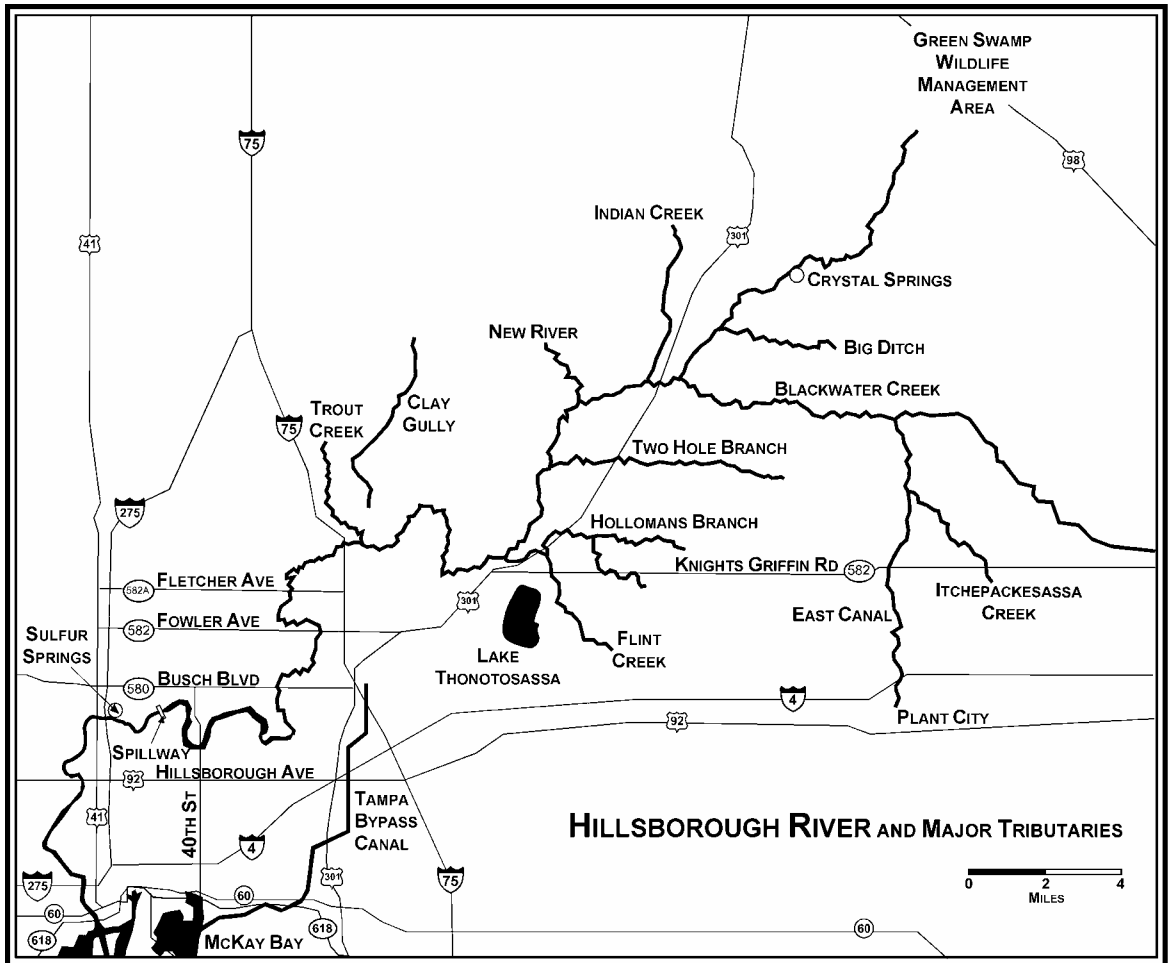
Following a southwesterly flow, the river moves through pine forests and swamps with palmetto undergrowth. These upper reaches of the river are

Figure 1 – Hillsborough River System



pristine. A variety of wildlife flourishes here including several threatened or endangered species such as the gopher tortoise, the bald eagle, the American alligator, and the Eastern indigo snake. The water is very clear and moves swiftly over a bottom substrate mostly composed of silt and mud with occasional limestone outcroppings. North of Hillsborough River State Park, rapids are present at a few spots along the river.

Figure 2 – Hillsborough River and Tributaries
(compiled from USGS Quadrangle Maps and a State of Florida Atlas)



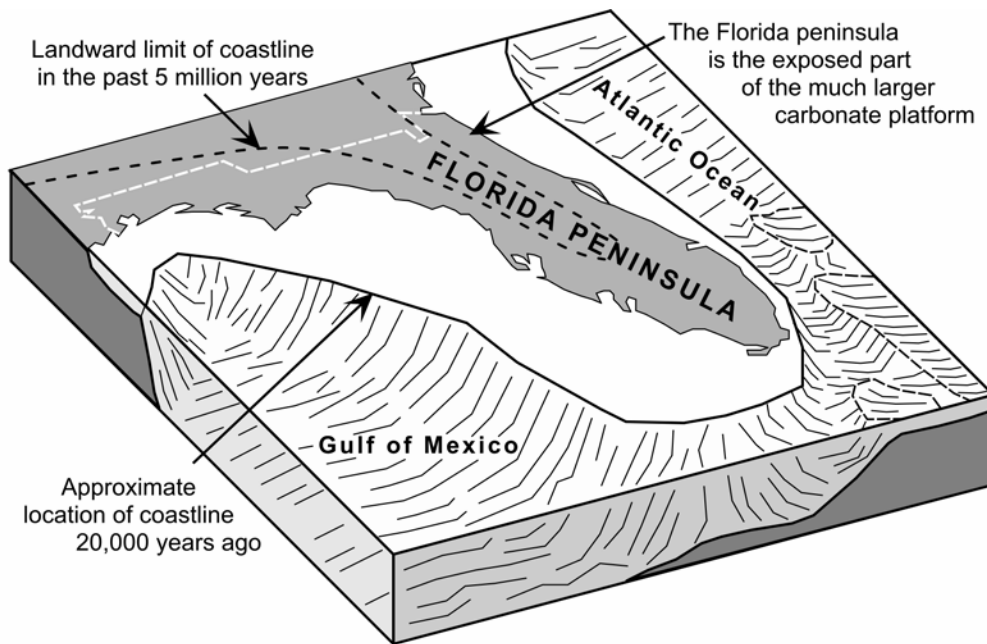
The State of Florida and Hillsborough County operate several parks in this region, including Hillsborough River State Park, where visitors can experience

the river and its wildlife through camping, canoeing, and hiking. The county parks provide similar activities and are open to the public year round. In this area, water is added to the river via two major tributaries, Flint Creek and Trout Creek. Near Trout Creek, a sinkhole connects the river to the underground Floridan Aquifer (Wolanksy and Thompson, 1987).

After it passes beneath Fletcher Avenue (CR 582), the Hillsborough River moves through a residential area and passes into the City of Temple Terrace. Here the river takes on a new appearance. Natural banks are replaced in some areas by riprapped or concrete walls, and storm drain outfalls empty directly into the river. The surrounding area here is mostly residential with a few county and city parks providing public boat access. After flowing through the City of Temple Terrace the river becomes a reservoir in Tampa just above a dam at 30th Street. This reservoir is a source of surface water for water treatment facilities that provide potable water for the City of Tampa. The dam restricts freshwater flow to the remainder of the river, especially during low flow periods. As it flows through the City of Tampa below the dam, the Hillsborough River is brackish. The water in this area is affected by tidal flows, stormwater and industrial run-off, and a major input, Sulphur Springs (The Florida Springs Task Force, 2000). Surrounded by skyscrapers, the Hillsborough river flows into Hillsborough Bay in downtown Tampa.

River water chemistry is influenced by factors including geology, land use, and water use (Berner and Berner, 1987). From its source in the Green Swamp to its confluence with Hillsborough Bay, the Hillsborough River flows over the

Figure 3 – Florida Carbonate Platform (Tihansky and Knochenmus, 2001)



limestone (CaCO_3) platform on which the entire State of Florida is situated (Figure 3) (Tihansky and Knochenmus, 2001). The regional geology is comprised of a sequence of limestone and dolomite layers underlying sand and clay (Tihansky and Knochenmus, 2001). The uppermost substrate of the river is mostly decaying organic matter/muds and sand. Weathering/ dissolution of this substrate and underlying regional platform affects the chemical composition of the water.

The river is fed by two major springs, Crystal Springs and Sulphur Springs. Crystal Springs is the largest freshwater source for the river. It is classified as a second magnitude spring (6.5 – 65 million gallons per day (MGD) flow) (Spechler, 1995) and, based on averages from 1923 – 1982, historically

contributed ~ 38 MGD of water to the river (Tihansky and Knochenmus, 2001). More recent measurements (1993 – 1994) indicate the flow has been reduced to ~ 24 MGD, little more than half the historical flow (Sepulveda, 2001). Prior to 1996, Crystal Springs and the surrounding land, though privately held, were open to the public as the Crystal Springs Recreation Preserve. Water was pumped out of the spring and trucked to the Zephyrhills drinking water bottling facility. In 1996 the owners of the land surrounding Crystal Springs closed the recreational facility to the public. Through an underground pipeline, pumping currently proceeds directly from the spring to the bottling facility, at more than 0.3 MGD. Recent changes to the water use permit allow pumping to incrementally increase over the next five years to an average daily withdrawal of over 0.75 MGD with a maximum of 1.1 MGD.

Sulphur Springs enters the river in the City of Tampa below the Hillsborough River Dam. Also classified as a second magnitude spring (The Florida Springs Task Force, 2000), it contributed ~ 27 MGD to the Hillsborough River between 1959 and 1982 (Wolanksy and Thompson, 1987). Like Crystal Springs, more recent measurements (1993 – 1994) indicate a reduced flow (~ 16 MGD) (Sepulveda, 2001). During times of low precipitation/ low river flow, one-third of the Sulphur Spring's flow is pumped into the Hillsborough River Reservoir (above the dam) to augment the city's drinking water supply (The Florida Springs Task Force, 2000). Beginning in the late 1800s, Sulphur Springs was a popular recreation area. The spring was purchased by the City of Tampa in 1957. A concrete pool was constructed, and the spring was operated as a public

recreation area until 1986 when it was closed indefinitely due to bacterial contamination (The Florida Springs Task Force, 2000). Plans for restoration of the spring are currently being considered.

In addition to inputs from two major springs, water is also added to the Hillsborough River by numerous natural and man-made tributaries. These tributaries, running through urban, agricultural, residential, and pristine lands (Figure 3 and Table 1), greatly affect the river's chemistry. The Hillsborough River's drainage basin includes areas north of Zephyrhills, east of Lakeland, and most of Hillsborough County (Figure 1).

The Hillsborough River can be divided into lower, middle, and upper sections according to land use. The lower brackish section runs through a highly industrialized area within the City of Tampa downstream from the Hillsborough River Dam (which restricts freshwater flow into this portion of the river). The middle river, just above the dam and northward to the edge of the City of Temple Terrace, is mostly residential. The upper river, from the edge of Temple Terrace north to its origin in the Green Swamp, is pristine and consists mostly of publicly held land (Florida Department of Natural Resources, 1989).

The Hillsborough River is vitally important to the surrounding area. Though considered a small river, it is the major source of freshwater for the City of Tampa. The Hillsborough River Reservoir holds 1.7 billion gallons of raw water. This water is supplied by the Hillsborough River, Sulphur Springs, and, during a recent drought (1999 – 2001), also from a sinkhole located near Morris Bridge Road. This sinkhole was connected to the reservoir via an above ground

pipeline (Tampa Bay Water, 2002; Southwest Florida Water Management District, 2002). Two facilities located on the river supply approximately 65 MGD of potable processed reservoir water to approximately 450,000 Tampa residents (Tippen, 1999 & 2000).

The depth of the river is insufficient for commercial shipping. Boat traffic is mostly recreational. Motorized boats are permitted on all parts of the river. However, some parts of the river are only accessible via kayak or canoe. The Southwest Florida Water Management District (SWFWMD), the Hillsborough County Environmental Protection Commission, the Florida Department of Environmental Protection, the Florida Fish and Wildlife Conservation Commission, and the United States Geological Survey (USGS) regularly monitor water quality and stream flow. These water quality data include pH, dissolved oxygen, turbidity, temperature, salinity, coliforms, and biological oxygen demand (BOD).

My investigation of the Hillsborough River was conducted from September 1999 until November 2001. During this period, the Hillsborough River Basin experienced drought conditions. For an eighteen month period between September 1999 and November 2001, rainfall totals were below the 1915 - 2001 historical average (Table 2). May and October 2000 rainfall totals were the lowest on record. The low rainfall totals led to a decrease in river flow. USGS measurements of streamflow of the Hillsborough River for the period between Sept. 1999 and Nov. 2001 are shown in Figure 4.

TABLE 1 – Hillsborough River Tributaries (input/output) ^a

| Tributary Name | General Description | Location of Intersection with Hillsborough River |
|---|---|--|
| Port Lonesome Ditches & Fish Hatchery Drain | Origin in swamps in E. Pasco/W. Polk counties, northwesterly flow | Intersect at various locations, near boundary of Hillsborough and Withlacoochee River in Pasco County |
| Zephyrhills Drain | Origin NW of Zephyrhills, flows S/SE receiving stormwater runoff from Zephyrhills | Intersects river 0.25 miles upstream of Crystal Springs |
| Big Ditch | Originates in swamps in NE Hillsborough County and Polk County, flows W through a phosphate processing area | Intersects the river approximately 1.25 miles downstream of Crystal Springs |
| Blackwater Creek | This watershed extends into Polk County, Receiving water from major tributaries: East Canal flows north, receiving city and agricultural runoff; Itchepackesassa Creek originates in Polk County, flowing northwest it receives runoff from agricultural and residential areas as well as industrial discharge. | Blackwater Creek, after being joined by its tributaries, flows westward through agricultural lands and intersects the river just upstream of Hillsborough River State Park |
| Indian Creek ^b | Originates approximately 2 miles west of Zephyrhills, flows S draining agricultural lands | Intersects river approximately 0.5 miles downstream from the US 301 intersect |
| Basset Branch & New River ^b | Origin in swamps N of SR 54 in Pasco County, flows S through agricultural lands | Both intersect the river within the boundaries of Hillsborough River State Park |
| Two Hole Branch ^b | South of Blackwater Creek extends west from SR 39, flows NW draining residential and agricultural lands, crossing US 301 | Intersects river approximately 1.75 miles west of the US 301 intercept |
| Hollomans Branch ^b | Extends from SR 39 near Plant City to US 301, NW flow receiving runoff from residential and agricultural lands | Intersects river approximately 1 mile downstream of US 301 |
| Cypress Creek including Thirteen & Seventeen Mile Run | Drains rural lands in Pasco and NW Hillsborough County | Main channel empties into the river |
| Trout Creek & Clay Gully West ^b | Originates in Pasco County near Cabbage Swamp, flows S through residential developments | Intersects river east of I-75 |
| Tampa Bypass Canal | Man-made structure with flow control system to alleviate flooding conditions for the cities of Temple Terrace and Tampa, originates near Trout Creek Park | Diverts flood waters from river, main canal drains into Palm River, small ditches drain into residential or commercial land areas |

^a Compiled from www.hillsboroughriver.org and Wolansky and Thompson, 1987.

^b Intermittent or non-perennial tributary

TABLE 2 - USGS Rainfall Data, Hillsborough River Drainage Basin (Sept. 1999- Nov. 2001) (Southwest Florida Water Management District, 2002a)

| Sampling Months | Rainfall Totals by Month (inches) | | | Historical Rainfall Average (inches) (1915 – 2001) |
|-----------------|-----------------------------------|-------|-------------------|---|
| | 1999 | 2000 | 2001 | |
| January | 3.27 ^a | 1.79 | 1.46 | 2.54 |
| February | 0.25 ^a | 0.66 | 0.72 | 2.98 |
| March | 1.21 ^a | 0.52 | 6.81 | 3.77 |
| April | 1.05 ^a | 1.33 | 0.22 | 2.57 |
| May | 3.58 ^a | 0.10 | 0.54 | 3.84 |
| June | 9.77 ^a | 8.17 | 8.51 | 7.66 |
| July | 4.84 ^a | 8.81 | 9.88 | 8.21 |
| August | 6.86 ^a | 7.38 | 6.48 | 8.12 |
| September | 4.57 | 7.01 | 12.15 | 6.94 |
| October | 4.14 | 0.05 | 1.27 | 2.92 |
| November | 2.33 | 1.70 | 0.33 | 1.91 |
| December | 1.58 | 1.12 | 1.05 ^a | 2.33 |
| Annual Totals | 43.44 | 38.63 | 49.43 | 53.86 |

^a These data, included for completeness, are not shown in Fig. 4, which represents rainfall only during the sampling period.

Although yearly rainfall totals (1999 – 2001) were below the historical averages, monthly precipitation was consistent with the normal pattern of increased rainfall in the summer months (beginning in April through September) and reduced rainfall in the winter months (Figure 5). Substantial variations in river chemistry were observed in conjunction with seasonal changes.

The objective of my thesis research, which principally involved measurements of the Hillsborough River’s major ion composition, was a

FIGURE 4 - Historical streamflow totals (open symbols, Δ) versus streamflow totals (closed symbols, \bullet) for sampling period (Sept. 1999 – Nov. 2001). A) USGS Monitoring station 02303000 located near Sampling station #3; B) USGS Monitoring Station 02303000 is located near Sampling Station #5; C) USGS Monitoring Station 02304500 is located near Sampling Station #9. (United States Geological Survey, 2003)

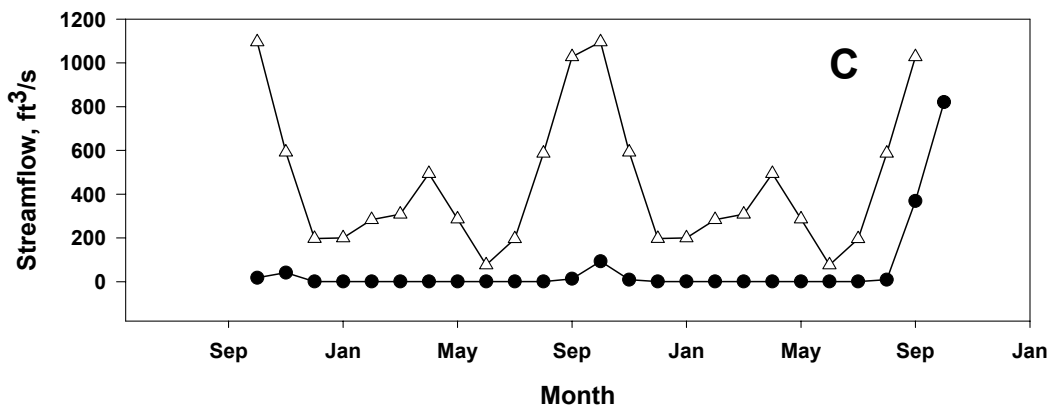
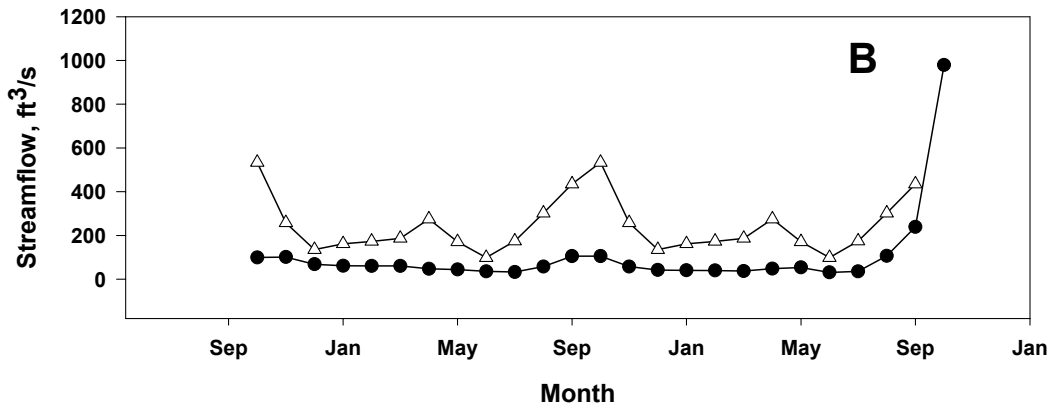
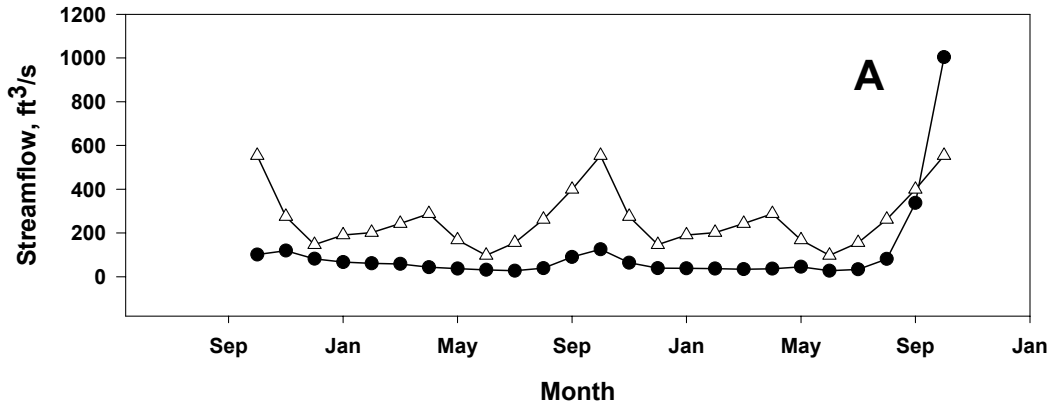
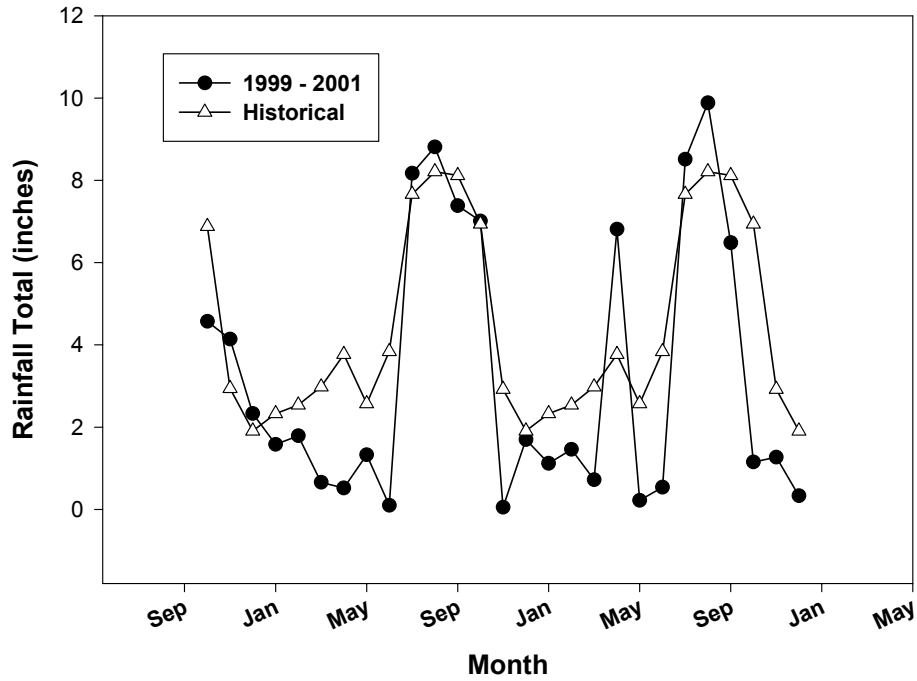


FIGURE 5 - USGS Rainfall Data for Hillsborough River Drainage Basin (09/1999 – 11/2001) versus historical averages for Sept. through Nov. (1912-2001). (Southwest Florida Water Management District, 2002)



characterization of both spatial and temporal variations in the river’s chemical composition. Observed variations in chemical composition provide insights into the river’s chemical sources, both natural and anthropogenic.

Sampling Strategies

Sampling locations were selected along approximately 54 miles of the river between the Green Swamp and Hillsborough Bay (Tampa Bay). Sampling locations 1-10 (Figure 1) are upstream stations, and sampling locations 11-13 are downstream from the dam. Individual sampling locations were chosen for accessibility as well as scientific interest. Stations 11-13 are affected by tidal flow, causing the water at these stations to be brackish. Station 1 was chosen because it is the closest accessible location to Crystal Springs, which provides the majority of the river's freshwater. Stations 2 and 6 are tributary stations, Blackwater Creek and Trout Creek. These locations provide insight into compositional differences between the tributaries and the river. The remaining sample sites were distributed at convenient sampling points along the river. Table 3 provides GPS coordinates and a location description of all 13 sampling locations.

Samples were collected monthly September 1999 through October 2000 and periodically thereafter. Shortly after sampling began, the Tampa Bay area experienced its worst drought in recorded history. Therefore, the majority of the samples were collected during unusually dry, low flow conditions.

At each sampling location, surface water samples were collected for analysis of major ions and phosphate. Spectrophotometric pH measurements

were conducted for a limited number of sampling dates at Stations 1-10. General observations with respect to flow, weather conditions, and water clarity were also recorded.

TABLE 3 - Hillsborough River System sampling locations

| Hillsborough River System Sampling Locations | | |
|--|--|---------------------------------|
| Location # | Description | GPS coordinates |
| 1 | Bridge, CR 39 near Crystal Springs | N 28°11'35.6" W 082°09'54.5" |
| 2 | Blackwater Creek, Bridge on CR 39 | N 28°08'22.0" W 082°08'58.7" |
| 3 | Hillsborough River State Park, US Hwy 301 | N 28°08'55.2" W 082°14'11.0" |
| 4 | John Sargent Park, US Hwy 301 | N 28°04'57.4" W 082°17'08.4" |
| 5 | Wilderness Park, Morris Bridge Rd. | N 28°05'57.0" W 082°18'43.1" |
| 6 | Trout Creek Park, Morris Bridge Rd. | N 28°05'16.5" W 082°20'56.2" |
| 7 | USF Riverfront Park, Fletcher Ave. | N 28°04'10.6" W 082°22'38.6" |
| 8 | Riverside Rotary Park, Fowler Ave. | N 28°03'16.4" W 082°21'51.4" |
| 9 | Florida College, Bullard Pkwy. | N 28°01'59.1" W 082°22'56.2" |
| 10 | Bridge, 40 th St. | N 28°00'31.7" W 082°24'51.9" |
| 11 | Lowry Park, Brevard St. | N 28°00'44.9" W 82°27'53.2" |
| 12 | Corner of N. Lee & Rivershore Dr. off of W. Hillsborough Ave. | N 27°59'49.6" W 82°28'11.9" |
| 13 | University of Tampa, W. Kennedy Blvd. | N 27°56'55.9" W 82°27'51.8" |

Materials and Methods

Major ions and phosphate

Preparation of Sample Bottles

Samples were collected in 250 mL low density polyethylene and Teflon bottles. All bottles were cleaned with Micro laboratory detergent and rinsed with deionized water. The bottles were then soaked for a minimum of 7 days in 4N hydrochloric acid. After removal from the acid, the bottles were triple rinsed with Milli-Q 18 M Ω cm high purity water and set to dry in a laminar flow hood within a clean room. Prior to use, acid cleaned bottles were stored in Fisher polyethylene bags. Polyethylene gloves were worn for all handling of bottles and at all times during the sampling process.

Sample Collection

Samples were collected from the bank of the river just below the surface via the following steps: 1) each bottle was removed from a Fisher polyethylene bag and submerged with cap in place; 2) the bottle was uncapped beneath the surface, filled, and recapped; 3) the bottle was then removed from the water and emptied. These steps were repeated twice before the final sample was collected. After sample collection the capped bottle was dried with a Kimwipe

and placed back in the polyethylene bag. Samples were transported to the laboratory within 6 hours of collection and refrigerated at $< 10\text{ }^{\circ}\text{C}$ until analysis.

Laboratory Analyses

Major ions

Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- , F^- , NO_3^- , and SO_4^{2-} were measured with a Dionex DX-500 ion chromatograph. As per EPA guidelines, anions were analyzed within 48 hours for NO_3^- and within 28 days for other anions (Pfaff, 1993).

Chromatographic analyses were performed using instrumental conditions recommended by Dionex, Appendix I. Prior to each analysis, the chromatograph was equilibrated for at least 30 minutes to promote instrumental stability. A 1 mL sub-sample was injected directly into the instrument's sample intake port. One disposable, sterile syringe was used for each sample and was then discarded. Ion concentrations were determined based on a 3-point calibration line. All standards were prepared in Milli-Q 18 M Ω cm high purity water. Standard concentrations and preparations are listed in Appendix II. The calibration line was determined prior to each sample run. Instrumental drift was monitored by periodically rerunning a standard solution.

Due to instrumentation difficulties, anion data were only obtained for nine of the nineteen sampling dates. Therefore, conclusions relating to general trends within the river are drawn only from the cation data. Carbonate alkalinity (CA) was calculated via cation/anion charge balance after determination of the other ions.

Phosphate

Samples were stored in the refrigerator ($< 10\text{ }^{\circ}\text{C}$) and analyzed for total phosphate (ΣPO_4) within 24 hours of collection. ΣPO_4 was measured spectrophotometrically following the technique described in Grasshoff et al. (1983). Reagents for the ΣPO_4 analysis were prepared as described in Appendix III.

A 30 mL sub-sample was removed from each bottle via syringe and then discarded. A second 30 mL sample was removed with the same syringe and utilized for analysis. One mL of ascorbic acid reagent and one mL of mixed reagent was added to each 30 mL sample. Five minutes was allowed for color development. Samples were transferred to a 10 cm spectrophotometric cell. Absorbance was measured on an HP 8453 spectrophotometer at a wavelength (λ) of 880 nanometers. To correct for the natural tannic color of the river water, each sample absorbance ($\lambda = 880\text{ nm}$) was measured against a baseline consisting of natural river water. Each sample was measured three times. Total phosphate concentrations (ΣPO_4) were determined based on a 3-point calibration line. Standards with concentrations of $0\text{ }\mu\text{M}$, $1\text{ }\mu\text{M}$, and $5\text{ }\mu\text{M}$ were prepared from a 10 mM PO_4^{3-} stock solution on the day of measurement and analyzed following the procedure described above. During periods of unusually high phosphate concentrations, this procedure was modified slightly. When exceptionally high phosphomolybdate absorbances were observed, a 1 cm spectrophotometric cell was used in place of the 10 cm cell and the calibration curve included standards at $15\text{ }\mu\text{M}$ and $25\text{ }\mu\text{M}$ phosphate.

Spectrophotometric pH

As with the major ions and phosphate samples, pH samples were collected manually from the bank of the river. Samples were collected in 10 cm spectrophotometric cells (volume $\approx 26 \text{ cm}^3$) as follows: 1) cells were submerged and filled without bubbles; 2) cells were capped with Teflon stoppers while submerged; 3) cells were removed from river and emptied. This process was repeated three times before a final sample was taken (Yao and Byrne, 2001). The cells were transported to the laboratory for immediate analysis. Samples for pH analyses were collected only from stations 1-10. The ionic strength at stations 11-13 is too high for freshwater pH measurement procedures (Yao and Byrne, 2001). More importantly, pH measurements at stations 11-13 were not of primary interest due to the strong influence of seawater on pH.

Spectrophotometric cells were returned to the laboratory and equilibrated at 25 °C for at least 30 minutes in a water-jacketed cell holder. Absorbances were measured with an HP 8453 diode array spectrophotometer: 1) each cell was removed from the thermostated holder and its optical surfaces were cleaned, 2) baseline absorbances were measured at 433, 558, and 730 nm, 3) using a Gilmont microburet, 0.2 mL of phenol red indicator was added to each cell, 4) cells were manually mixed, 5) absorbances were again measured at 433, 558, and 730 nm. The pH was calculated using the following equations (Yao and Byrne, 2001):

$$\text{pH} = \text{pK}_1 + \log\left(\frac{R - e_1}{e_2 - Re_3}\right)$$

$$e_1 = 0.00244, e_2 = 2.734, e_3 = 0.1075$$

$$R = \left(\frac{558 A^{-730} A}{433 A^{-730} A} \right)$$

and

$$pK_1 = pK_1^\circ - 4A \left[\left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} \right) - 0.3\mu \right]$$

$$pK_1^\circ = 8.034 \text{ at } 25^\circ \text{C and } A = 0.5092 \text{ at } 25^\circ \text{C}$$

μ = ionic strength calculated from major ion concentrations (see Appendix IV)

CaCO₃ Saturation State

The CaCO₃ saturation state (Ω) was calculated from the major ion data following these steps.

- 1) Activity coefficients (γ) were calculated using the following equation, (Stumm and Morgan, 1981):

$$\log \gamma_i = -0.509 Z_i^2 \left[\frac{\mu^{1/2}}{(1 + \mu^{1/2})} - 0.3\mu \right]$$

where Z_i is the charge of ion "i".

- 2) The HCO₃⁻ dissociation constant (K_2') at each ionic strength was calculated from the following equation:

$$K_2' = K_2^\circ \left(\frac{\gamma_{HCO_3^-}}{\gamma_{H^+} \gamma_{CO_3^{2-}}} \right)$$

where K_2° is the HCO₃⁻ dissociation constant at zero ionic strength,

$$(K_2^\circ = 10^{-10.329})$$

- 3) The concentration of CO_3^{2-} was then calculated from the following equation:

$$[\text{CO}_3^{2-}] = \text{CA} \left(2 + \frac{[\text{H}^+]}{K_2} \right)^{-1}$$

where $K_2' = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ and $\text{CA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] = \text{carbonate alkalinity}$.

- 4) The $\text{CaCO}_{3(s)}$ solubility product for each sample (K_{sp}') was calculated as:

$$K_{sp}' = K_{sp}^\circ (\gamma_{\text{Ca}^{2+}} \gamma_{\text{CO}_3^{2-}})^{-1}$$

where $K_{sp}^\circ = 10^{-8.48}$ (Smith and Martell, 2001).

- 5) Finally, the saturation state (Ω) was calculated as follows:

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}'}$$

Saturation state (Ω) was only calculated for the sampling dates and locations where the pH was determined.

Results/Discussion

Spatial Distributions

Originating in the Green Swamp and flowing through a progressively more urbanized environment, the Hillsborough River water has a diverse set of geochemical influences. These influences on the evolving composition of the river as it flows from its source waters to Hillsborough Bay (Figure 6, Table 4) are described below.

At Station 1, concentrations of the major ions are comparable to or somewhat lower than concentrations observed on other parts of the river. Water here is derived mostly from the Green Swamp, but during times of high precipitation, sources may include water from the Withlacoochee River Basin (Wolanksy and Thompson, 1987). The average concentrations of Na^+ , K^+ , Cl^- , SO_4^{2-} , and ΣPO_4 (Table 4) are slightly elevated over groundwater levels seen at Crystal Springs (Table 5). These elevated ion concentrations at Station 1 suggest possible inputs from sea-salt aerosols and/or agricultural run-off.

Crystal Springs, located downstream from Station 1, provides a major input to the river directly from the aquifer. The major ion concentrations here are low with the exception of Ca^{2+} and CA which reflect the spring's origins within the Karstian aquifer (Table 5). Measured concentrations of Na^+ (243 μM), K^+ (9.9 μM), F^- (7.5 μM), SO_4^{2-} (96 μM), and ΣPO_4^{3-} (1.2 μM) are lower

TABLE 4 – Average concentrations of major ions at sampling locations in this study ^a (see Appendices V, VI, and VII for complete raw data)

| # | Na ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | Cl ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ | CA ^b | PO ₄ ³⁻ |
|----------------|-----------------------|----------------|------------------|------------------|-----------------|----------------------|-------------------------------|------------------------------|-----------------|-------------------------------|
| 1 | 278 | 22 | 146 | 1449 | 11.6 | 264 | 150 | 10.2 | 2564 | 5.1 |
| 2 | 2120 | 344 | 288 | 1092 | 25 | 1684 | 696 | 30.2 | 2288 | 14 |
| 3 | 500 | 65 | 189 | 1375 | 19 | 457 | 174 | 70 | 2690 | 5.6 |
| 4 ^d | 509 | 64 | 194 | 1330 | 20 | 540 | 257 | 38 | 2475 | 5.8 |
| 5 | 504 | 64 | 194 | 1385 | 21 | 439 | 262 | 34 | 2612 | 6.5 |
| 6 | 478 | 58 | 217 | 1481 | 20 | 443 | 404 | 28 | 2755 | 5.1 |
| 7 | 451 | 56 | 213 | 1479 | 28 | 392 | 573 | 14 | 2145 | 4.6 |
| 8 ^d | 411 | 52 | 201 | 1371 | 26 | 410 | 506 | 12 | 2044 | 5.3 |
| 9 | 430 | 56 | 197 | 1360 | 21 | 406 | 477 | 7.7 | 2062 | 5.7 |
| 10 | 909 | 66 | 256 | 1461 | 21 | 1242 | 588 | 0 | 2019 | 4.8 |
| 11 | 61 x 10 ³ | 1285 | 6900 | 3348 | NA ^c | 64 x 10 ³ | 4391 | NA | NA | 5.0 |
| 12 | 100 x 10 ³ | 2107 | 11383 | 3909 | NA ^c | 125 | 6945 | NA | NA | 5.4 |
| 13 | 255 x 10 ³ | 5501 | 27435 | 6600 | NA ^c | 298 | 14106 | NA | NA | 5.3 |

^a All concentrations given in µM and include only data from this study (9/99 – 11/01)

^b CA (carbonate alkalinity) is calculated from charge balance (CA = [HCO₃⁻] + 2[CO₃²⁻]), and at typical river pH [HCO₃⁻] >> [CO₃²⁻].

^c Due to required dilution of samples, this parameter is below the instrument detection limit.

^d Due to unreliability of data, Sept. 1999 data are excluded for Station 8 and Jan. 2000 data are excluded for Station 4.

than those at other locations on the river (Table 4). However, the NO₃⁻ concentration measured in Crystal Springs is substantially higher than NO₃⁻ in other parts of the river. Station 1 is the only location with major ion concentrations closely comparable to Crystal Springs.

Blackwater Creek enters the Hillsborough River below Crystal Springs. Among the various Hillsborough River tributaries, the water chemistry of Blackwater Creek (Station 2) is quite unique. The mean concentrations of most major ions (except Ca^{2+} and Ca) are substantially higher than the Hillsborough River average (Figure 6, Table 4). The average Na^+ concentration (2120 μM) is almost four times the mean for the mid-river (stations 3-9) (469 μM), while K^+ , 344 μM , is almost six times the mean mid-river value. Phosphate averages 14 μM in Blackwater Creek compared to 5.5 μM in the mid-river.

Enrichment of ions in this tributary is a result of inputs that are unique to the area surrounding Blackwater Creek. Blackwater Creek is itself fed by three tributaries: Tiger Creek, East Canal, and Itchepackesassa Creek (Florida Department of Environmental Protection, 2002). East Canal receives stormwater runoff from Plant City. Itchepackesassa Creek drains an area agricultural rangeland and receives industrial discharge (Morgan and Denson, 1995). From Figure 6 and Table 4, it is seen that substantial dilution at the confluence of Blackwater Creek and the Hillsborough River decreases downstream concentrations of Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , and ΣPO_4 to much lower levels.

Major ions concentrations in the river immediately downstream of Blackwater Creek are essentially stable. Ion concentrations at stations 3,4, and 5 show little variation (Table 4, Figure 6). The exception to this is NO_3^- , which originates in Crystal Springs. As water moves downstream, NO_3^- decreases steadily. Station 6 is located on another tributary of the river, Trout Creek. At

this location, water samples are enriched in Mg^{2+} , Ca^{2+} , and SO_4^{2-} , while phosphate, K^+ , Na^+ , and Cl^- are similar to concentrations upstream. F^- shows an increase between Stations 6 and 7 and SO_4^{2-} shows a large increase

FIGURE 6 - Average concentrations of major ions in the Hillsborough River by sampling station.

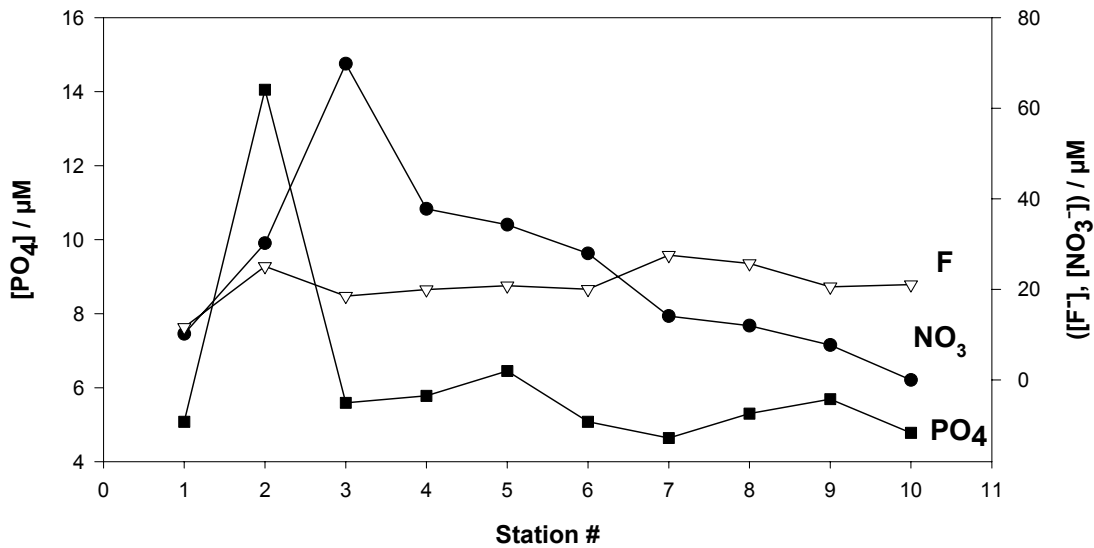
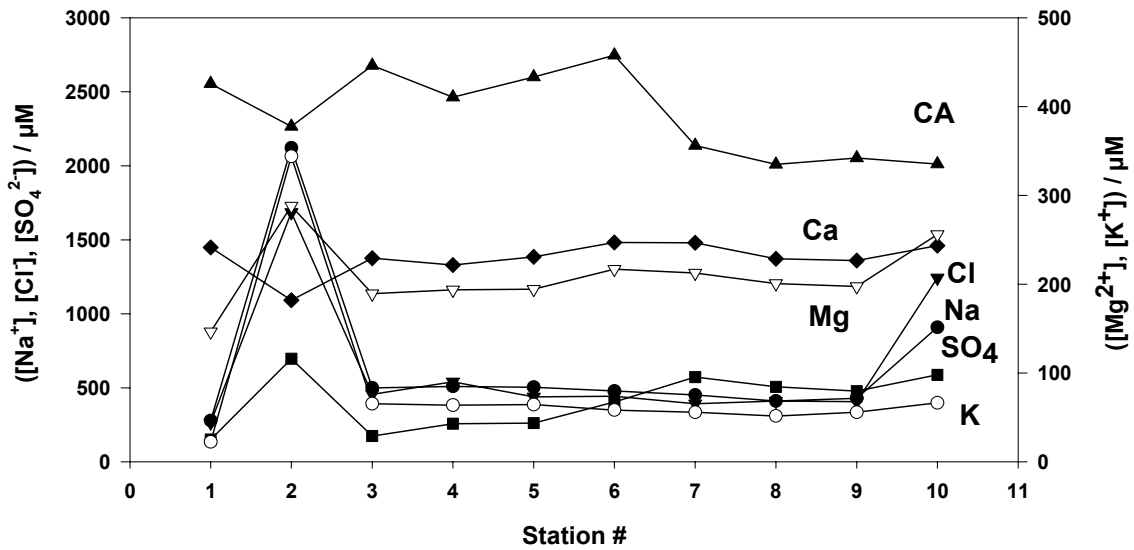


TABLE 5 - Comparison of Hillsborough River water, spring water, and ground water^a

| Location | Na ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | Cl ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ | HCO ₃ ⁻ | Reference |
|---|-----------------|----------------|------------------|------------------|----------------|-----------------|-------------------------------|------------------------------|-------------------------------|--------------------------------|
| Crystal Springs | 243 | 9.9 | 172 | 1533 | 7.5 | 308 | 96 | 150 | 3003 | This study |
| Crystal Springs | 233 | NA | 172 | 1569 | NA | 274 | 94 | 60.6 | 2328 | (Champion and Starks, 2001) |
| HR – Station 1 | 278 | 22 | 146 | 1449 | 11.6 | 264 | 150 | 10.2 | 2564 ^b | This study (mean 9/99 – 11/01) |
| Florida Groundwater (Polk City)^c | 139 | 12.8 | 230 | 848 | 5.3 | 127 | 25 | NA | 2033 | Back & Hanshaw, 1970 |
| HR – Stations 3-9 | 469 | 59 | 201 | 1396 | 22 | 444 | 375 | 29.5 | 2396 ^b | This study (mean 9/99 – 11/01) |
| Florida Groundwater (Plant City)^c | 522 | 21 | 453 | 1646 | 21 | 339 | -- ^d | NA | 4000 | Back & Hanshaw, 1970 |
| Sulphur Springs | 13913 | 248 | 1506 | 3516 | NA | 16338 | 2081 | 14.4 | 2443 | (Champion and Starks, 2001) |

^a All concentrations expressed in µM; when necessary data were converted from original (wt/wt) concentrations (e.g. ppm)

^b CA (carbonate alkalinity) concentrations are based on charge balance and as such are actually [HCO₃⁻] + 2[CO₃²⁻]. At typical river pH, [HCO₃⁻] >> [CO₃²⁻].

^c Groundwater samples taken from different depths, but considered part of the same hydrologic unit by the author; The Polk City sample is considered to be drawn from water that feeds many of the springs in the area.

^d Value actually listed as zero.

between Stations 5 and 7. A possible explanation for the variations seen at Stations 6 and 7 is groundwater seepage. The USGS determined that the specific conductance of groundwater here is greater than that of the local surface water. A sinkhole near Trout Creek may allow groundwater to seep into the surface water, especially during low flow conditions (Wolanksy and Thompson, 1987). Further investigation is required to unambiguously determine the mechanism for the significantly increased levels of F^- measured at Station 7.

At stations 8 and 9, major ion concentrations, with the exception of SO_4^{2-} , are near the levels measured in Stations 3-5. F^- concentrations between Stations 8 and 9 decrease to levels approximately equal to those measured at Station 5. ΣPO_4 is near the average concentration encountered on the river.

Concentrations of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , F^- , K^+ , and SO_4^{2-} at Station 10 are higher than those observed at Stations 8 and 9, and ΣPO_4 decreases slightly. Concentration changes are greatest for Na^+ and Cl^- : 430 μM and 406 μM at Station 9 compared to 909 μM and 1242 μM at Station 10. Station 10 is located near the reservoir for the City of Tampa's drinking water treatment facility (Fig. 1). During times of low flow or low precipitation, this reservoir is augmented with water pumped from Sulphur Springs (Florida Springs Task Force, 2000). During the drought between Sept. 1999 and Nov. 2001, augmentation of the surface water supply and the flow of the Hillsborough River became a necessity. Water was pumped into the reservoir from a sinkhole located on Morris Bridge Rd., the Tampa Bypass Canal, and also from Sulphur Springs (Tampa Bay Water, 2002; Southwest Florida Water Management District, 2002). Ion concentrations are

enriched in Sulphur Springs and in other groundwater sources in this area (Table 5), and likely account for the increased ion concentrations at Station 10.

Dissolved ΣPO_4 is low in groundwater. Consequently, increased groundwater pumping into the river may account for the reduced ΣPO_4 concentrations at Station 10.

The Hillsborough River water below the Hillsborough River Dam is composed of inputs from Sulphur Springs, flow over the dam, and tidal mixing from Hillsborough Bay. The concentrations of most ions at Stations 11-13 (Table 4) are several orders of magnitude higher than those seen at Stations 1 - 10. Flow over the dam is variable and can be non-existent at times of very low precipitation. Table 6 compares the ion concentrations in the river below the dam with the waters of Sulphur Springs and seawater.

TABLE 6 - Comparison of major ion concentrations in the Hillsborough River (Stations 11-13) to seawater and Sulphur Springs.^a

| River Location | Na ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | Cl ⁻ | SO ₄ ²⁻ | Reference |
|-----------------------------|------------------------|----------------|------------------|------------------|-----------------|------------------------|-------------------------------|--------------------------------|
| HR – Stations 11-13 | 139 x 10 ³ | 2960 | 15200 | 4620 | NA ^c | 169 x 10 ³ | 8772 | This study (mean 9/99 – 11/01) |
| Seawater^b | 481 x 10 ³ | 10500 | 54100 | 10700 | 70 | 562 x 10 ³ | 28900 | (Byrne, 2002) |
| Sulphur Springs | 13.9 x 10 ³ | 248 | 1506 | 3516 | NA ^c | 16.3 x 10 ³ | 2081 | (Champion and Starks, 2001) |

^a All concentrations expressed in μM .

^b S=35, density = 1.0248 kg/L used to convert original data from $\mu\text{M}/\text{kg}$ to μM for comparison

^c Data not available.

Temporal Variations

Ions concentrations in the river exhibit substantial temporal changes. Due to difficulties with anion concentration measurements for a portion of the sampling period, the following discussion principally explores trends for the cation data. Ca^{2+} and Mg^{2+} show a similar temporal pattern (Figure 7). This similarity may indicate a similar source for these cations. Na^+ and K^+ also show a similar temporal pattern in the river (Figure 8). Since this study occurred during a drought period, changes in ion concentrations before and after Tropical Storm Gabrielle (Sept. 2001) were especially dramatic. Concentrations of all major cations, except K^+ dropped by approximately 50 percent.

Figure 9 depicts the concentration of ΣPO_4 in the Hillsborough River throughout the sampling period. As a tributary with greatly enhanced concentrations, Blackwater Creek (Station 2) is shown separately. ΣPO_4 levels measured at Stations 3-10 approached those found in Blackwater Creek only on September 19, 2001. Station 1 and Station 10 are also show separately. Ion concentrations at Station 1 are generally distinct from trends in ion concentrations observed in the remainder of the river. Due to inputs previously discussed, ion concentration trends at Station 10 are distinct from those in the mid-river.

In concert with seasonal changes in precipitation and river flow, phosphate concentrations generally rise in June and peak in September. While phosphate

Figure 7 – Ca^{2+} and Mg^{2+} average concentrations (μM), Stations 3-9, throughout the sampling period. Error bars represent the total concentration range (minimum and maximum) for Stations 3-9 for each sampling date.

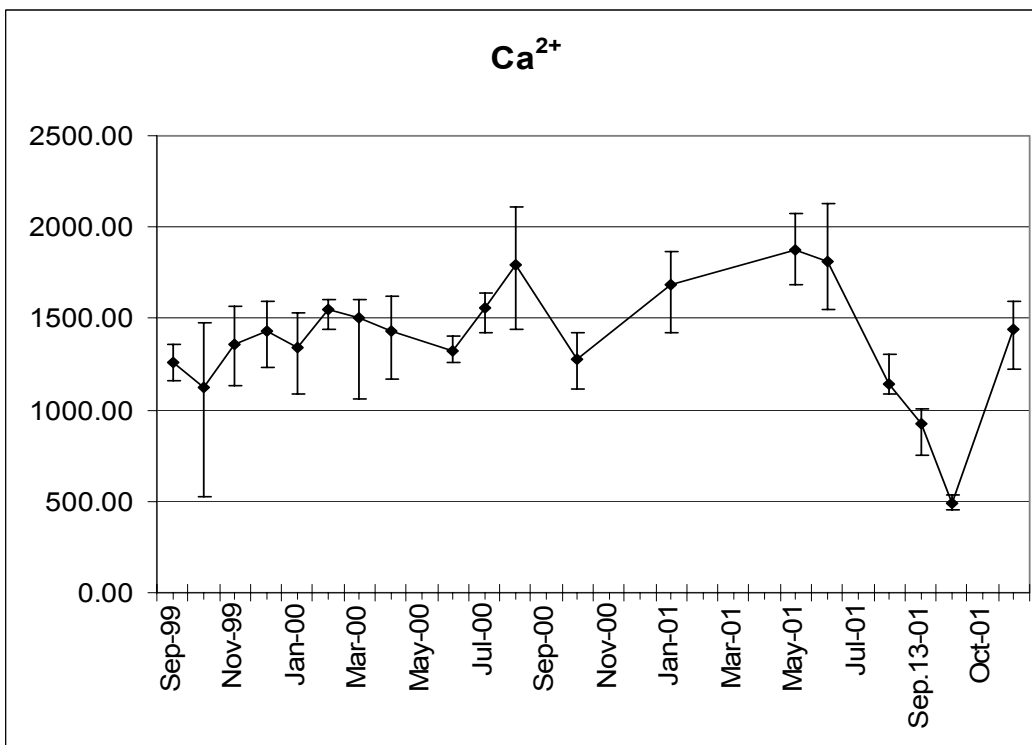
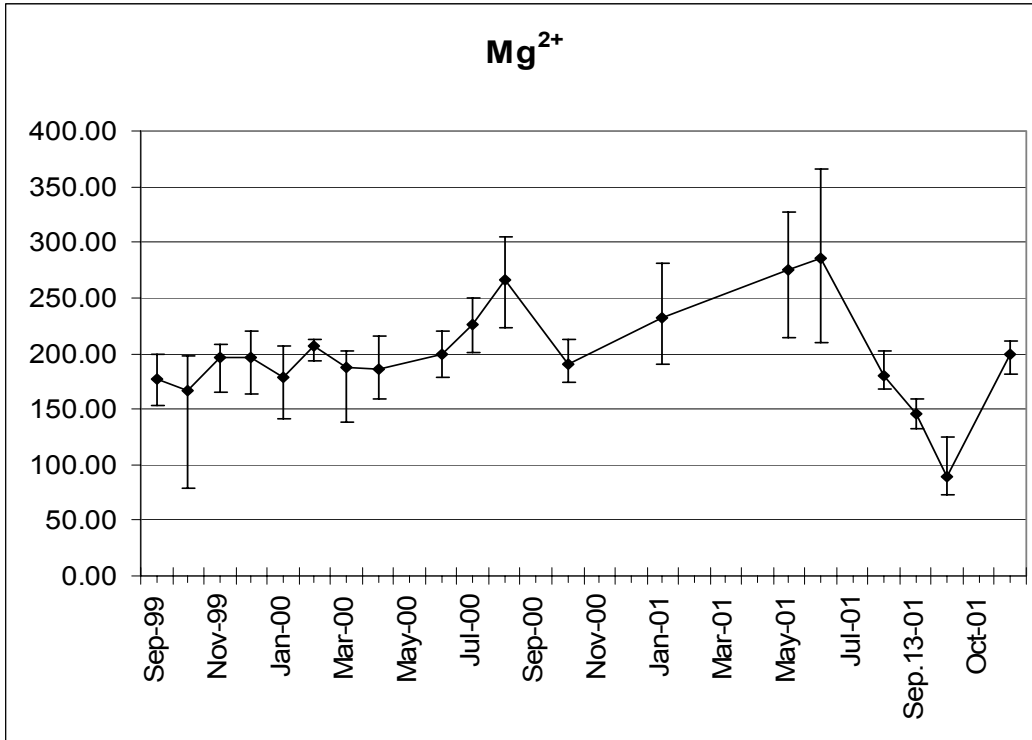
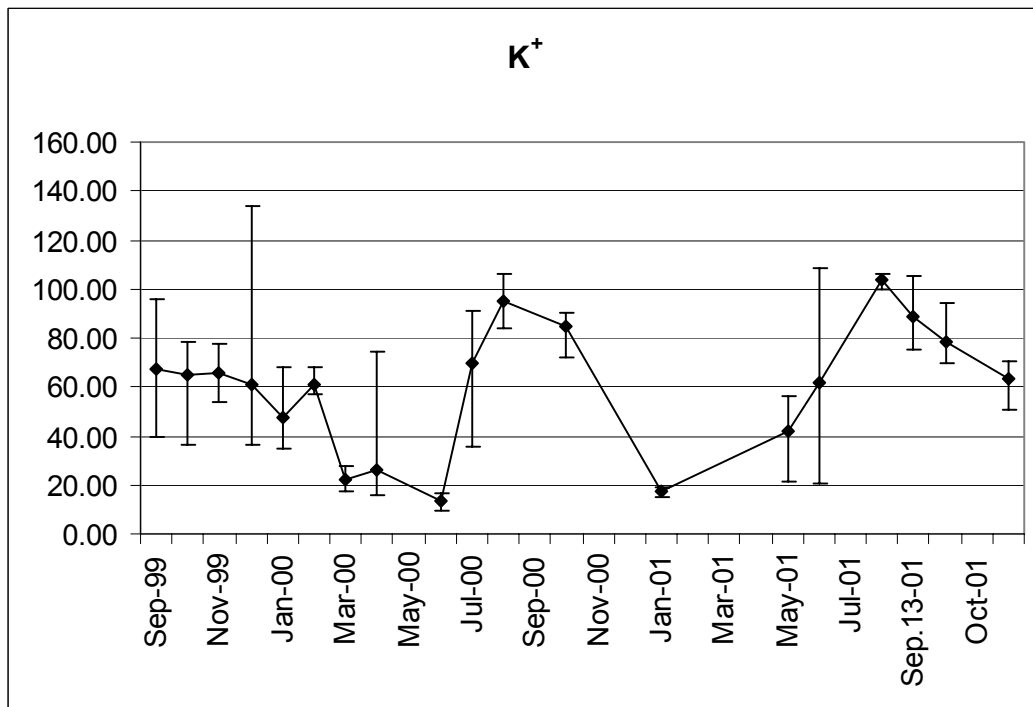
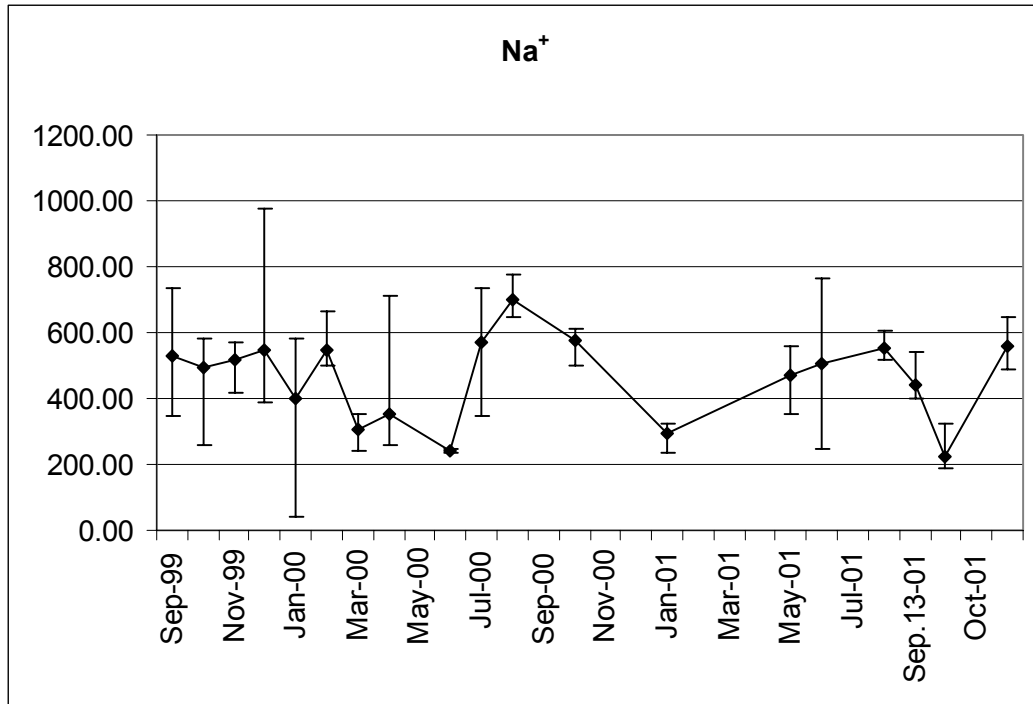


Figure 8 – Na⁺ and K⁺ average concentrations (µM), Stations 3-9, throughout the sampling period. Error bars represent the total concentration range (minimum and maximum) for Stations 3-9 for each sampling date.



concentrations in the river are strongly dependent on precipitation and flow conditions, Blackwater Creek does not show this same pattern. Agricultural and industrial inputs to this tributary may override seasonal effects. No definitive trends or patterns are seen in Blackwater Creek, as noted, and ΣPO_4 concentrations here (Station 2) are consistently higher than the remainder of the river. Only during maximum flow conditions do phosphate concentrations in the river approach those seen in Blackwater Creek.

Phosphate concentrations are generally low at Station 1 and a seasonal peak was seen in 2001 but not during 2000. The low phosphate concentrations at Station 1 may reflect the swampy, undeveloped surrounding area. Agricultural and industrial inputs here are generally low. The exceptional phosphate concentrations in September 2001 may be attributable to the effects of Tropical Storm Gabrielle which brought 2-5 inches of rain to the basin in the period Sept. 13-15, 2001. At high water stages, the headwaters of the river may have been connected to the Withlacoochee River basin or other surrounding surface waters (Wolanksy and Thompson, 1987).

Large temporal changes are also seen in river pH. During the measurement period, spectrophotometrically determined pH in the river ranged from a low of 6.52 to a high of 8.805, Table 7. Rainfall in Florida has a slightly acidic pH, while the average pH of Florida groundwater is between 7 and 8 (Champion and Starks, 2001). Water that has been in contact with the limestone substrate for an extended period of time will tend toward saturation with respect to CaCO_3 and high river pH. Conversely, water with $\Omega < 1$ and low pH indicates

a low contact time with the substrate and points to recent precipitation as a causative factor. Figure 10 shows an inverse relationship between the average spectrophotometric pH and rainfall between May and November (2001). Figure 11 shows the Ω values calculated for the sampling stations in the same time period. The river is supersaturated for the months of May and June 2001 due to low precipitation. Increases in precipitation during the months of August, September, and November create CaCO_3 undersaturation. A complete table with the calculated Ω values can be found in Appendix VIII.

TABLE 7 - Spectrophotometric pH measurements by sampling station,
T = 25 ° C.

| # | May 2001 | June 2001 | Aug 2001 | Sept 2001 ^a | Nov 2001 |
|---------|----------|-----------|----------|------------------------|-----------------|
| 1 | 7.394 | 7.482 | 6.975 | 6.686 | 7.375 |
| 2 | 7.388 | 7.773 | 7.256 | 6.638 | 7.308 |
| 3 | 7.892 | 7.76 | 7.290 | 6.852 | 7.573 |
| 4 | 8.066 | 7.931 | 6.782 | 6.570 | 7.208 |
| 5 | 8.085 | 7.891 | 6.778 | 6.525 | 7.304 |
| 6 | 8.010 | 7.755 | 6.751 | NA ^b | 7.263 |
| 7 | 7.908 | 7.719 | 6.646 | 6.521 | 7.289 |
| 8 | 7.858 | 7.727 | 6.690 | 6.541 | NA ^b |
| 9 | 7.905 | 7.614 | 6.698 | 6.584 | 7.249 |
| 10 | 7.986 | 8.390 | 7.000 | 6.769 | 7.793 |
| Average | 7.849 | 7.804 | 6.886 | 6.630 | 7.373 |

^a September 2001 data applies to the sampling date Sept. 19, 2001

^b Sampling sites inaccessible on these dates due to heavy rainfall.

Riverine Input Mechanisms

Cationic and anionic concentrations in the river have the following order: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$. While this follows the general order of other North American rivers (Table 8), the Hillsborough River is distinctive in a number of respects. The average mid-river HCO_3^- concentration, 2396 μM , is more than two times the North American average. The average Ca^{2+} concentration (Stations 3 to 9), 1396 μM , is more than two times the North American average and seven times the world average. Na^+ and Cl^- are also somewhat enriched in the Hillsborough River compared to North American and World Rivers. The Na^+ average (Stations 3-9) (469 μM) is close to the Actual North American average reported by Berner and Berner (1987) (365 μM), but greater than the Mean World Rivers value of 161 μM given by Markich and Brown (1998). The average (Stations 3-9) Cl^- concentration was also enriched, 444 μM (HR) compared to 260 μM cited by Berner and Berner (1987) and 110 μM (Mean World Average) reported by Markich and Brown (1998).

The average SO_4^{2-} concentration in the river is double the North American average reported by Berner and Berner (1987) and greater than seven times the world average (Markich and Brown, 1998). K^+ concentrations in the Hillsborough River are nearly double the Mean World Rivers reported by Markich and Brown (1998) and higher than the North American average of 38 μM reported by Berner and Berner (1987). Phosphate concentrations in the Hillsborough River are several times greater than those seen in North American

FIGURE 9 - Concentration of ΣPO_4^{3-} in the Hillsborough River showing correlation between rainfall totals and ΣPO_4^{3-} concentration. (A) Stations 3-9 (B) Station 1, Blackwater Creek (Station 2), and Station 10.

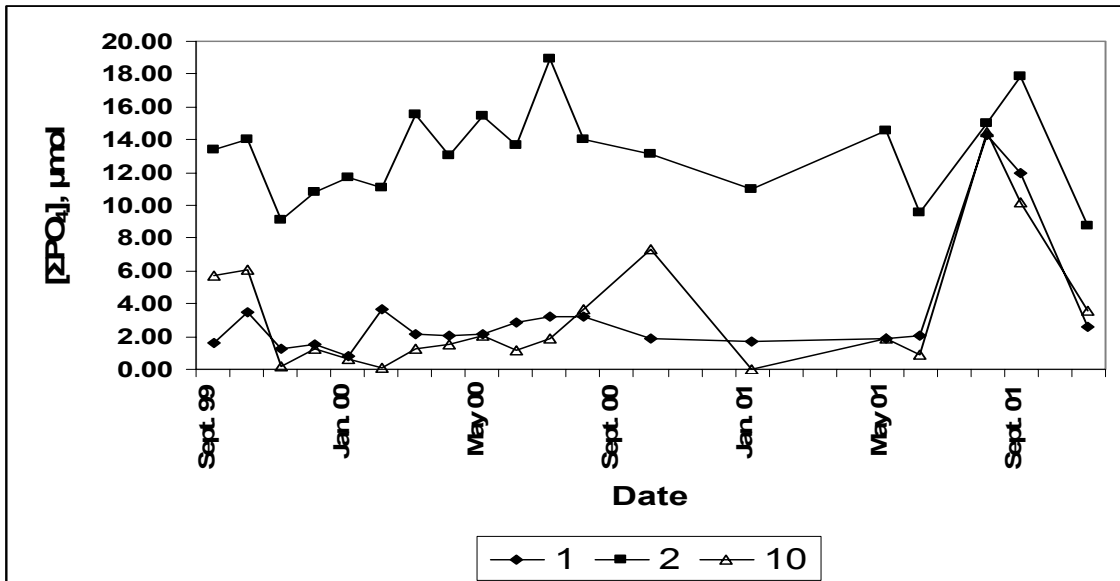
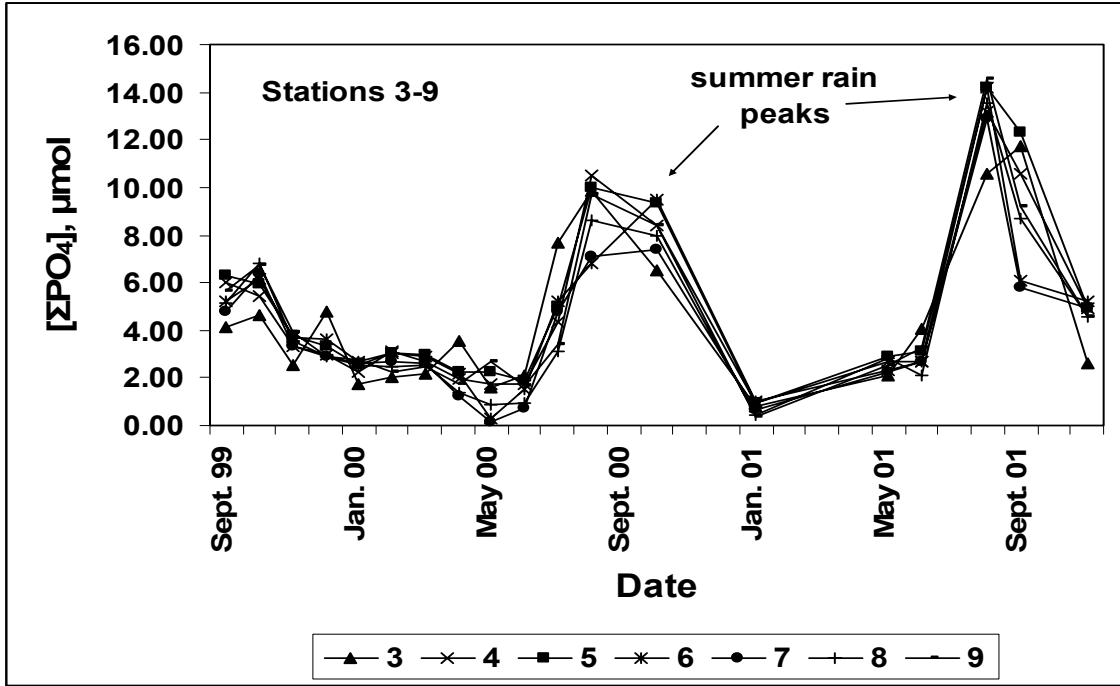


FIGURE 10 – Relationship between spectrophotometric pH and rainfall measurements for the time period May 2001 – Nov. 2001 (this study, (Southwest Florida Water Management District, 2002)).

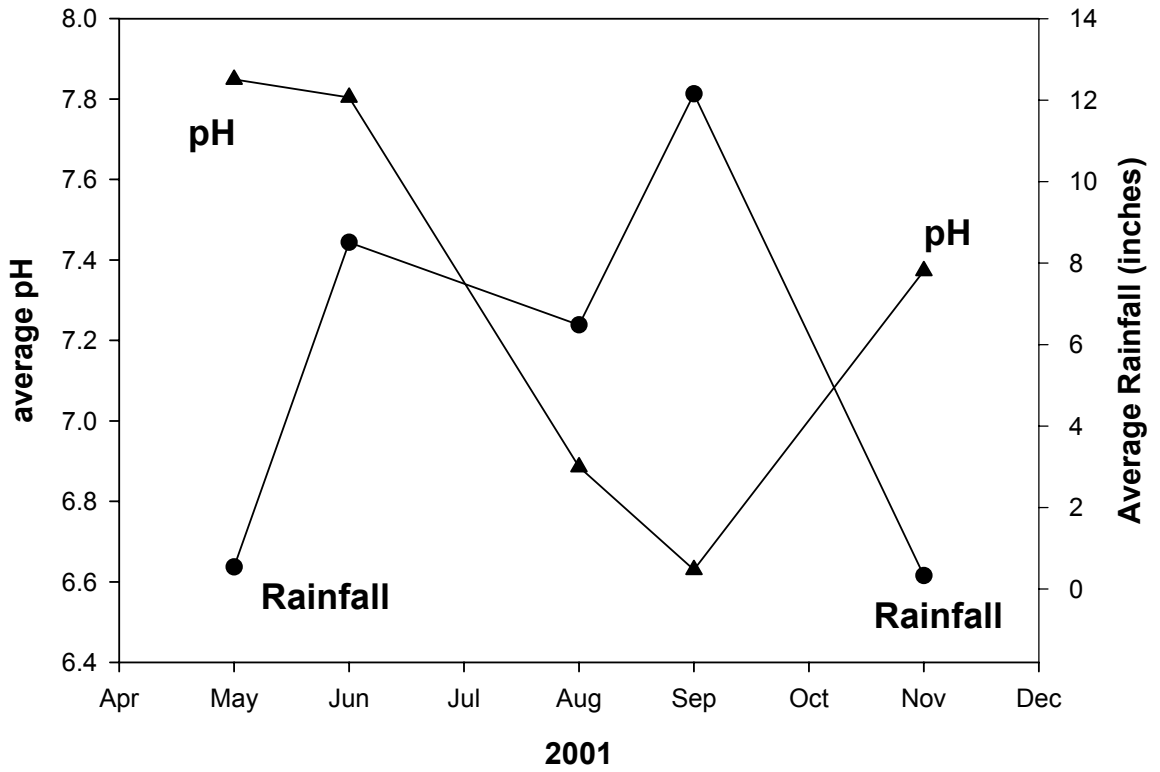
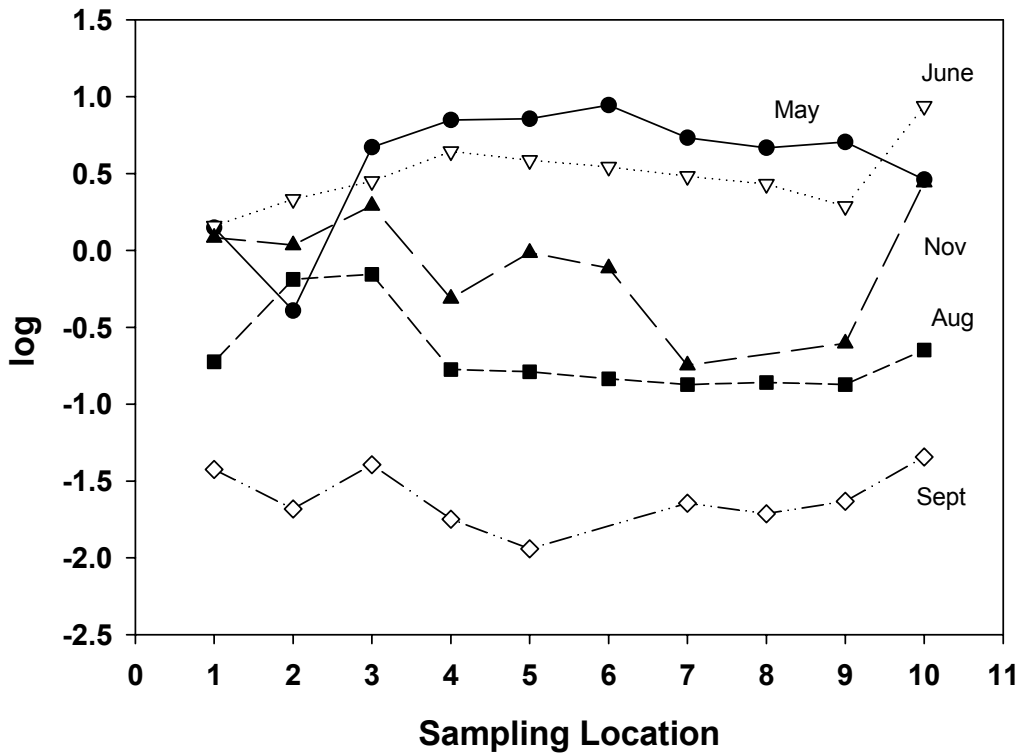


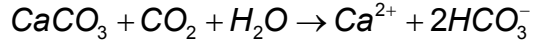
Figure 11 – CaCO₃ saturation state (Ω) by sampling location.



and World river averages.

Differences between the Hillsborough River and North American and World Rivers are attributable to a variety of influences. Some of the complex processes that deliver ions to the Hillsborough River are unique to the Hillsborough River basin, while others are common to most rivers.

Ca²⁺ and the CA in the Hillsborough River are primarily influenced by the CaCO₃ composition of the Florida platform (Figure 2). As illustrated by the following process:



the expected $\text{HCO}_3^- / \text{Ca}^{2+}$ ratio for dissolution of pure limestone is 2 (Drever, 1997). Samples taken from Crystal Springs show a CA / Ca^{2+} molar concentration ratio equal to approximately 2.1 (Table 5). Groundwater samples from Polk City and Plant City show similar ratios, ~ 2.4 . Due to the important contributions of $\text{CaCO}_{3(s)}$ to the composition of the Hillsborough River, the average CA / Ca^{2+} ratio is also close to 2 (Figure 12). This relationship suggests that most of the alkalinity in the river can be attributed to the dissolution of CaCO_3 . (For pure limestone, $\Delta\text{CA} / \Delta\text{Ca}^{2+} \sim 2$, e.g. the dissolution of CaCO_3 adds 2 mols of alkalinity per mol of Ca^{2+} (see above equation)).

Na^+ and Cl^- concentrations in the river are substantially higher than seen in groundwater samples. Na^+ and Cl^- averaged 463 μM and 444 μM in the river, but in Florida groundwater, Na^+ and Cl^- concentrations average less than half that of the river. One spring that shows an exception to this is Sulphur Springs. The Na^+ (5000 μM) and Cl^- (5726 μM) concentrations here are greatly enriched.

Na^+ and Cl^- in the river are strongly correlated (Figure 13). The calculated $\text{Cl}^- / \text{Na}^+$ molar ratio for Stations 1-9 is 0.68 ± 0.007 . This ratio is somewhat smaller than that observed at Crystal Springs (0.78). At Station 10 the $\text{Cl}^- / \text{Na}^+$ ratio is 1.27 ± 0.04 , and at Stations 11-13, the ratio is 1.23 ± 0.06 (Figure 13). Berner and Berner (1987) calculated that in world rivers 8% of the Na^+ and 13% of the Cl^- is a product of atmospheric sea salt. They attributed the majority of the Na^+ and Cl^- , 42% and 57%, to the dissolution of evaporates (halites). Another Na^+ and Cl^- enrichment mechanism is run-off including

FIGURE 12 - Relationship between Ca^{2+} and CA (carbonate alkalinity) in the Hillsborough River; $r^2=0.978$, slope 1.93 ± 0.05 ; \blacktriangle represents outlying data points that were not considered when calculating the regression. These points are labeled with the station number where each sample was collected. They are from Aug. 2000 (#4,5) and June 2000 (#2).

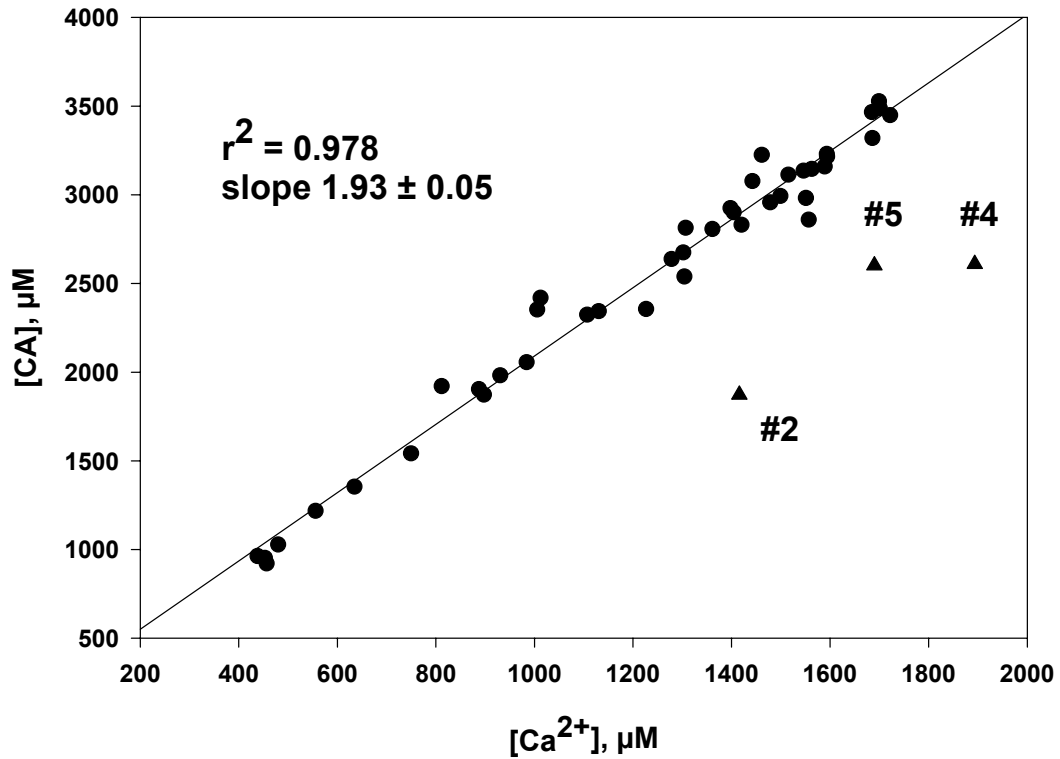


TABLE 8 - Comparison of major ion concentrations in the Hillsborough River to Mean concentrations in North America and World Rivers ^a

| River Location | Na ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | PO ₄ ³⁻ | Reference |
|---------------------------------------|-----------------|----------------|------------------|------------------|-----------------|-----------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------|
| HR – Stations 3-9 ^b | 469 | 59 | 201 | 1396 | 22 | 444 | 375 | 2396 ^c | 5.5 | This study (mean 9/99 – 11/01) |
| Mean World Rivers | 161 | 26 | 99 | 200 | NA ^d | 110 | 50 | NA ^d | 0.1 | Markich & Brown, 1998 |
| N. America River Average | 365 | 38 | 202 | 529 | NA ^d | 260 | 187 | 1185 | NA ^d | Berner & Berner, 1987 |
| Average World Rivers | 230 | 38 | 128 | 332 | NA ^d | NA ^d | NA ^d | NA ^d | NA ^d | Chester, 1990 |

^a All concentrations expressed in µM; when necessary data were converted from original (wt/wt) concentrations (e.g. ppm).

^b Water at Station 1 consists of swamp water from a pristine area and is not representative of the mid river average and Station 2, Blackwater Creek, also has unique water chemistry. Station 10 is greatly influenced by input from Sulphur Springs as well as supplemental water from the Tampa Bypass Canal. These stations are considered separately and therefore excluded here.

^c CA (carbonate alkalinity) concentrations are based on charge balance and as such are actually [HCO₃⁻] + 2[CO₃²⁻]. However, at typical river pH CA ≈ [HCO₃⁻]

^d Data not reported in original source

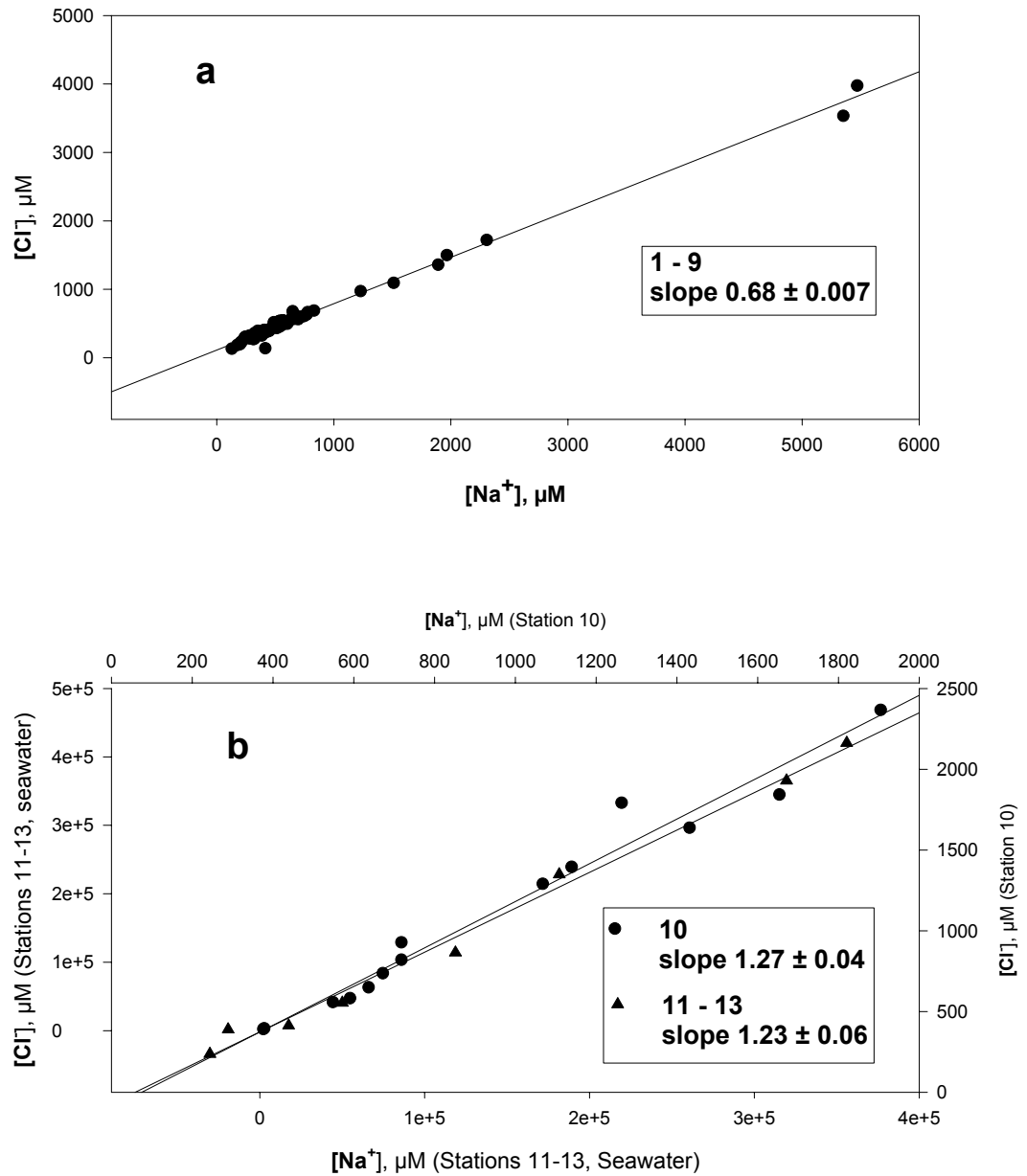
domestic effluent (Berner and Berner, 1987). Rainwater enriched in sea-salt aerosols is one important source of Na^+ and Cl^- to Florida rivers (Madsen et al., 1992). The Hillsborough River receives inputs from stormwater outfalls and may also receive septic system leachate both directly and through historically contaminated groundwater inputs (Florida Springs Task Force, 2000). Saline groundwaters are an important source of Na^+ and Cl^- , and this source is may be especially important in the area downstream of the Sulphur Springs outfall. In the coastal transition zone, seawater intrusion plays a role in the ionic make-up of the groundwater. The molar ratio $\text{Cl}^- / \text{Na}^+$ in Sulphur Springs water is ~ 1.17 , closely matching that of seawater (~ 1.15) The calculated ratios at Station 10 and 11-13 also closely match that of Sulphur Springs and seawater.

Riverine SO_4^{2-} concentrations can be influenced by a variety of sources, some which are unique to the Hillsborough River drainage basin. Dissolution of gypsum (CaSO_4), a by-product of the large phosphate mining and processing industry in Florida may be an especially significant source of SO_4^{2-} . Other anthropogenic influences in the area include agricultural run-off and industrial emissions. SO_4^{2-} enrichment is also a natural result of chemical weathering, biological processes, and sea-salt deposition.

Riverine K^+ concentrations are affected by agricultural run-off. Agricultural interests, extensive in Florida, utilize fertilizers rich in K^+ . Another source of K^+ is the substantial amount of leaf litter/decaying organic matter in the river. K^+ is more readily released from plant matter than most other ions (Berner and Berner,

1987) . The release of K^+ from organic rich muds should be especially important in times of high precipitation.

FIGURE 13 - Correlation between concentrations of Na^+ vs. Cl^- at (a) Stations 1-9 ($r^2=0.991$) and (b) Station 10 ($r^2 = 0.993$) and 11-13 ($r^2 = 0.972$).



Summary and Overview of Hillsborough River Chemistry

This study identified a variety of unique inputs to the Hillsborough River. Limestone dissolution is the major controlling factor for calcium and carbonate concentrations in the river. The river's major freshwater source, Crystal Springs, is the dominant source of nitrate (NO_3^-) to the river. Due presumably to microbial respiration, NO_3^- steadily decreases downstream of this source. The mid-river stretch of the Hillsborough River (Stations 3 to 9) exhibited a fairly constant major ion composition. Blackwater Creek is a dominant source of ΣPO_4 to the river. Saline groundwater from Sulphur Springs and possible sinkhole linkages contribute major ions near the Hillsborough River dam (Station 10). Downstream of the Hillsborough River Dam (Stations 10-13), the water chemistry more closely resembles that of seawater than the mid-river water. Flow over the dam is extremely low at times of low precipitation. This portion of the river is also tidally influenced.

The ionic composition of the river varies seasonally. Major ions were lowest at times of highest precipitation. This, however, was not the case for ΣPO_4 which exhibited high concentrations with increased precipitation. Seasonal variations were also seen in pH and CO_2 system chemistry. The river's pH decreased dramatically during periods of high precipitation. Changes in pH

induced by precipitation created large variations in the river's CaCO_3 saturation state. During low precipitation, the river is supersaturated with respect to CaCO_3 . Periods of high precipitation produce strong CaCO_3 undersaturation.

In conclusion, the chemistry of the Hillsborough River is influenced by complex interactions of many natural and anthropogenic inputs. Temporal variations in the river's chemistry is identified as a particularly important area for future work. Chemical measurements of particular importance include phosphate, nitrate (and other nitrogenous species), solution pH, and associated CO_2 system parameters.

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Appendices

Appendix I - Dionex DX-500 Ion Chromatograph specifications

| Cation Analysis | | |
|-----------------|---|------------|
| Column | Eluent | Flow rate |
| IonPac CS12A | 20 mM methylsulfonic acid (MSA) | 1.0 mL/min |
| Anion Analysis | | |
| Column | Eluent | Flow rate |
| IonPac AS14 | 3.5 mM Na ₂ CO ₃ / 1.0 mM NaHCO ₃ | 1.2 mL/min |

Appendix II - Standard concentrations for cation and anion analyses

| Cations ^a | Standard 1 | | Standard 2 | | Standard 3 | |
|-------------------------------|------------|-----|------------|-----|------------|-----|
| | µM | ppm | µM | ppm | µM | ppm |
| Na ⁺ | 217 | 5 | 870 | 20 | 2175 | 50 |
| K ⁺ | 26 | 1 | 102 | 4 | 256 | 10 |
| Mg ²⁺ | 41 | 1 | 165 | 4 | 411 | 10 |
| Ca ²⁺ | 125 | 5 | 499 | 20 | 1248 | 50 |
| Anions ^b | Standard 1 | | Standard 2 | | Standard 3 | |
| | µM | ppm | µM | ppm | µM | ppm |
| F ⁻ | 10.5 | 0.2 | 42.1 | 0.8 | 105 | 2 |
| Cl ⁻ | 141 | 5 | 564 | 20 | 1410 | 50 |
| NO ₃ ⁻ | 16.1 | 1 | 64.5 | 4 | 161 | 10 |
| SO ₄ ²⁻ | 52 | 5 | 208 | 20 | 520 | 50 |

^a Cation standards were prepared from VHG Labs (Manchester, NH) Water Pollution Standard 5 containing: K⁺, Mg²⁺ at 100 µg/mL (ppm); Ca²⁺, Na⁺ at 500 µg/mL (ppm).

^b Anion standards were prepared from a VHG Labs (Manchester, NH) IC Custom Standard 1 containing: Cl⁻, SO₄²⁻ at 50.0 µg/mL (ppm); NO₃⁻ at 10 µg/mL (ppm); F⁻ at 2.0 µg/mL (ppm).

Appendix III - Reagent Preparation for ΣPO_4 analysis

- 1) ascorbic acid reagent – 5 g of ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) was dissolved in 25 mL Milli-Q water, 25 mL 4.5 M H_2SO_4
- 2) mixed reagent – Part 1 – 12.5 g ammonium heptamolybdate tetrahydrate was dissolved in 125 mL Milli-Q water, Part 2 -- 0.5 g potassium antimony tartrate was dissolved in 20 mL Milli-Q water; Part 1 was added to 350 mL H_2SO_4 and stirred continuously, Part 2 added and mixed well.

Reagent 1 was prepared monthly, while reagent 2 remained stable for several months.

Appendix IV – Calculated Ionic Strength for each sampling station^a

| Station # | 06/20/2000 | 7/24/2000 | 8/22/2000 | 5/02/2001 | 6/25/2001 | 8/27/2001 | 09/13/2001 | 09/19/2001 | 11/19/2001 |
|-----------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 1 | 4.83×10^{-3} | 5.44×10^{-3} | 5.75×10^{-3} | 6.22×10^{-3} | 5.69×10^{-3} | 3.69×10^{-3} | 2.54×10^{-3} | 2.17×10^{-3} | 6.19×10^{-3} |
| 2 | 13.4×10^{-3} | 6.47×10^{-3} | 5.94×10^{-3} | 4.34×10^{-3} | 13.34×10^{-3} | 7.71×10^{-3} | 5.27×10^{-3} | 2.32×10^{-3} | 8.64×10^{-3} |
| 3 | 4.73×10^{-3} | 6.10×10^{-3} | 6.02×10^{-3} | 6.24×10^{-3} | 6.40×10^{-3} | 5.44×10^{-3} | 3.81×10^{-3} | 2.08×10^{-3} | 6.11×10^{-3} |
| 4 | 5.00×10^{-3} | 6.35×10^{-3} | 7.56×10^{-3} | 6.38×10^{-3} | 6.48×10^{-3} | 4.81×10^{-3} | 3.54×10^{-3} | 2.29×10^{-3} | 5.15×10^{-3} |
| 5 | 5.13×10^{-3} | 5.87×10^{-3} | 8.47×10^{-3} | 6.39×10^{-3} | 6.47×10^{-3} | 4.68×10^{-3} | 4.13×10^{-3} | 1.97×10^{-3} | 6.08×10^{-3} |
| 6 | 5.18×10^{-3} | 6.93×10^{-3} | 6.72×10^{-3} | 7.66×10^{-3} | 9.06×10^{-3} | 4.56×10^{-3} | 3.69×10^{-3} | NA | 5.77×10^{-3} |
| 7 | 5.01×10^{-3} | 6.94×10^{-3} | 9.49×10^{-3} | 8.54×10^{-3} | 8.57×10^{-3} | 4.83×10^{-3} | NA | 2.19×10^{-3} | 2.32×10^{-3} |
| 8 | 5.15×10^{-3} | 6.49×10^{-3} | 9.32×10^{-3} | 8.17×10^{-3} | 7.97×10^{-3} | 4.68×10^{-3} | 4.04×10^{-3} | 2.01×10^{-3} | 2.16×10^{-3} |
| 9 | 5.13×10^{-3} | 6.50×10^{-3} | 8.37×10^{-3} | 8.11×10^{-3} | 7.54×10^{-3} | 4.57×10^{-3} | 3.96×10^{-3} | 2.09×10^{-3} | 2.60×10^{-3} |
| 10 | 8.66×10^{-3} | 8.54×10^{-3} | 8.07×10^{-3} | 10.18×10^{-3} | 8.44×10^{-3} | 4.14×10^{-3} | 3.85×10^{-3} | 2.40×10^{-3} | 6.19×10^{-3} |

^a Stations 11-13 excluded from this appendix. The calculated ionic strength is based on a calculated Carbonate Alkalinity (CA). Since CA is a minor constituent in seawater, it cannot be calculated for Stations 11-13 which exhibit seawater like characteristics.

Appendix V – Cation concentrations in the Hillsborough River (µM)

| Station # | Cations | 09/19/1999 | 10/23/1999 | 11/21/1999 | 12/20/1999 | 01/20/2000 | 02/21/2000 | 03/20/2000 | 04/17/2000 | 06/20/2000 |
|-----------|---------|-------------------|------------|------------|------------|--------------------|------------|------------|------------|------------|
| 1 | Na | 296.2 | 278.8 | 276.8 | 282.4 | 238.7 | 288.3 | 280.6 | 214.6 | 282.7 |
| | K | 14.32 | 11.77 | 8.87 | 13.69 | 9.15 | 11.99 | 12.34 | 7.34 | 9.46 |
| | Mg | 149.4 | 148.1 | 152.3 | 155.4 | 127.4 | 158.9 | 155.5 | 118.6 | 148.5 |
| | Ca | 1661.8 | 1645.8 | 1648.1 | 1670.0 | 1345.2 | 1717.2 | 1688.2 | 1279.9 | 1304.5 |
| 2 | Na | 1400.2 | 1415.0 | 3260.8 | | | | | 2260.7 | 5470.2 |
| | K | 235.6 | 235.8 | 526.5 | NA | NA | NA | NA | 242.7 | 767.6 |
| | Mg | 223.0 | 256.7 | 348.8 | | | | | 339.5 | 339.4 |
| | Ca | 873.1 | 995.3 | 1491.8 | | | | | 1025.4 | 1415.9 |
| 3 | Na | 345.8 | 503.3 | 515.64 | 975.0 | 332.7 | 513.7 | 302.7 | 711.7 | 242.7 |
| | K | 39.9 | 57.0 | 57.1 | 133.5 | 36.4 | 57.7 | 17.5 | 74.27 | 9.72 |
| | Mg | 153.5 | 197.90 | 201.7 | 191.8 | 141.3 | 201.7 | 191.1 | 216.4 | 179.0 |
| | Ca | 1173.5 | 1480.86 | 1569.2 | 1277.6 | 1104.4 | 1569.3 | 1595.0 | 1625.8 | 1278.3 |
| 4 | Na | 636.8 | 511.5 | 523.1 | 589.7 | 41.0 ^a | 666.2 | 294.3 | 294.9 | 247.1 |
| | K | 81.3 | 70.6 | 64.8 | 57.0 | 5.13 ^a | 60.1 | 18.7 | 16.7 | 9.97 |
| | Mg | 186.8 | 170.3 | 193.2 | 199.6 | 14.4 ^a | 203.8 | 192.2 | 186.6 | 182.3 |
| | Ca | 1263.8 | 1074.4 | 1329.5 | 1409.4 | 114.6 ^a | 1519.5 | 1587.0 | 1541.2 | 1361.1 |
| 5 | Na | 735.5 | 552.4 | 549.2 | 388.0 | 580.0 | 498.5 | 298.2 | 305.9 | 249.7 |
| | K | 95.7 | 69.6 | 69.7 | 36.8 | 68.4 | 58.3 | 19.3 | 18.1 | 11.0 |
| | Mg | 198.7 | 193.8 | 207.9 | 163.4 | 195.1 | 193.4 | 192.8 | 186.6 | 183.1 |
| | Ca | 1334.7 | 1310.2 | 1430.6 | 1234.2 | 1460.1 | 1436.4 | 1583.3 | 1537.1 | 1404.3 |
| 6 | Na | 460.6 | 579.8 | 417.4 | 458.9 | 529.2 | 537.2 | 324.5 | 297.4 | 239.7 |
| | K | 55.5 | 76.7 | 54.1 | 48.4 | 54.2 | 63.1 | 26.0 | 19.6 | 13.3 |
| | Mg | 169.9 | 190.1 | 165.2 | 219.5 | 207.3 | 212.0 | 199.2 | 184.8 | 220.5 |
| | Ca | 1259.0 | 1245.6 | 1133.4 | 1596.5 | 1533.9 | 1603.8 | 1599.2 | 1507.0 | 1305.7 |
| 7 | Na | 468.0 | 566.3 | 513.4 | 462.4 | 447.7 | 585.6 | 329.7 | 258.2 | 241.4 |
| | K | 56.8 | 78.8 | 66.7 | 47.1 | 45.3 | 67.9 | 26.8 | 15.9 | 15.9 |
| | Mg | 184.3 | 178.2 | 200.3 | 196.0 | 177.8 | 211.1 | 194.7 | 158.8 | 214.8 |
| | Ca | 1358.9 | 1191.2 | 1360.8 | 1492.1 | 1305.3 | 1593.4 | 1546.3 | 1322.1 | 1260.8 |
| 8 | Na | 40.5 ^a | 257.5 | 535.0 | 469.2 | 353.5 | 537.9 | 350.5 | 320.1 | 234.9 |
| | K | 6.14 ^a | 36.1 | 71.4 | 50.3 | 34.7 | 60.8 | 27.9 | 19.7 | 16.9 |
| | Mg | 13.6 ^a | 78.2 | 201.1 | 199.3 | 146.5 | 209.1 | 201.8 | 190.3 | 211.5 |
| | Ca | 97.3 ^a | 521.0 | 1342.2 | 1492.3 | 1083.6 | 1567.2 | 1569.7 | 1169.7 | 1305.2 |

Appendix V – Cation concentrations in the Hillsborough River (µM) (continued)

| Station # | Cations | 09/19/1999 | 10/23/1999 | 11/21/1999 | 12/20/1999 | 01/20/2000 | 02/21/2000 | 03/20/2000 | 04/17/2000 | 06/20/2000 |
|-----------|---------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 9 | Na | 521.1 | 485.4 | 571.5 | 484.9 | 497.2 | 507.2 | 243.4 | 286.2 | 239.2 |
| | K | 73.2 | 68.6 | 77.4 | 51.8 | 47.6 | 56.8 | 17.9 | 19.7 | 16.9 |
| | Mg | 164.6 | 157.6 | 200.9 | 204.7 | 205.7 | 211.2 | 138.9 | 172.7 | 204.1 |
| | Ca | 1160.2 | 1033.2 | 1330.0 | 1508.6 | 1532.7 | 1562.7 | 1056.9 | 1341.4 | 1318.2 |
| 10 | Na | 534.6 | 533.2 | 562.1 | 525.7 | 563.1 | 529.3 | 1183.7 | 2031.6 | 2590.3 |
| | K | 80.8 | 80.8 | 63.3 | 54.3 | 54.5 | 45.8 | 43.1 | 57.5 | 64.7 |
| | Mg | 158.8 | 176.5 | 257.1 | 261.1 | 273.1 | 208.8 | 307.0 | 435.9 | 197.5 |
| | Ca | 1086.1 | 1131.3 | 1598.3 | 1631.6 | 1752.1 | 1263.5 | 1497.3 | 1897.7 | 1547.0 |
| 11 | Na | | 60157.2 | | | | | | | 121053.9 |
| | K | | 1253.3 | NA | NA | NA | NA | NA | NA | 2506.5 |
| | Mg | NA | 6624.2 | | | | | | | 13700.9 |
| | Ca | | 4815.6 | | | | | | | 3942.3 |
| 12 | Na | 82384.5 | 90040.1 | | | | | | | 171598.1 |
| | K | 1739.2 | 1867.1 | NA | NA | NA | NA | NA | NA | 3529.6 |
| | Mg | 9339.6 | 10203.7 | | | | | | | 20242.8 |
| | Ca | 4641.0 | 4616.0 | | | | | | | 5040.2 |
| 13 | Na | 189867.1 | 344022.6 | | | | | | | 315227.2 |
| | K | 3989.9 | 7596.2 | NA | NA | NA | NA | NA | NA | 6496.5 |
| | Mg | 20983.3 | 32503.6 | | | | | | | 28224.7 |
| | Ca | 5564.2 | 8358.7 | | | | | | | 7734.9 |

^a Data not included in mean calculations due to unreliability.

Appendix V – Cation concentrations in the Hillsborough River (µM) (continued)

| Station # | Cations | 07/24/2000 | 08/22/2000 | 10/04/2000 | 01/30/2001 | 05/02/2001 | 06/25/2001 | 08/27/2001 | 09/13/2001 |
|-----------|------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 1 | Na ⁺ | 313.9 | 323.9 | 293.8 | 298.3 | 385.9 | 314.4 | 288.3 | 175.9 |
| | K ⁺ | 18.72 | 11.64 | 9.69 | 16.13 | 14.7 | 12.02 | 73.85 | 72.86 |
| | Mg ²⁺ | 147.8 | 156.9 | 147.1 | 167.4 | 176.5 | 160.5 | 149.8 | 105.9 |
| | Ca ²⁺ | 1499.0 | 1589.2 | 1527.1 | 1868.7 | 1685.8 | 1550.8 | 930.8 | 634 |
| 2 | Na ⁺ | 1965.7 | 1511.5 | 1594.4 | 993.4 | 830.2 | 5352.5 | 1892.2 | 1229.0 |
| | K ⁺ | 270.9 | 241.3 | 274.6 | 208.3 | 142.3 | 960.7 | 326.8 | 237.7 |
| | Mg ²⁺ | 262.4 | 262.3 | 271.3 | 342.5 | 245.6 | 386.9 | 321.3 | 251.6 |
| | Ca ²⁺ | 1005.5 | 1012.3 | 1024.8 | 1231.6 | 811.7 | 1397.8 | 1306.9 | 887.5 |
| 3 | Na ⁺ | 675.9 | 696.2 | 564.2 | 323.1 | 351.6 | 748.6 | 603.7 | 404.8 |
| | K ⁺ | 90.28 | 102.5 | 80.9 | 19.18 | 21.68 | 108.7 | 99.83 | 102.1 |
| | Mg ²⁺ | 211.7 | 223.5 | 210.9 | 190.0 | 213.7 | 213.3 | 202.4 | 154.8 |
| | Ca ²⁺ | 1478.6 | 1442.1 | 1425.5 | 1585.9 | 1700.7 | 1546.2 | 1302.1 | 897.6 |
| 4 | Na ⁺ | 602.0 | 776.9 | 501.1 | 323.7 | 421.8 | 701.9 | 566.1 | 538.4 |
| | K ⁺ | 72.43 | 105.5 | 72.3 | 18.39 | 34.79 | 93.39 | 103.5 | 105.2 |
| | Mg ²⁺ | 213.9 | 283.2 | 183.8 | 198.5 | 222.2 | 212.4 | 190.6 | 159.5 |
| | Ca ²⁺ | 1556.7 | 1689.7 | 1116.0 | 1627.0 | 1699.3 | 1593.7 | 1130.5 | 749.5 |
| 5 | Na ⁺ | 676.6 | 768.2 | 577.6 | 315.7 | 450.4 | 763.1 | 562.9 | 473.6 |
| | K ⁺ | 82.31 | 106.0 | 85.41 | 16.36 | 39.7 | 103.4 | 102.4 | 92.77 |
| | Mg ²⁺ | 200.6 | 305.3 | 213.0 | 197.6 | 223.5 | 210.2 | 179.9 | 155.5 |
| | Ca ²⁺ | 1420.1 | 1893.7 | 1337.2 | 1623.9 | 1684.9 | 1562.7 | 1107.1 | 984.4 |
| 6 | Na ⁺ | 736.8 | 651.2 | 614.4 | 284.8 | 448.0 | 518.9 | 534.3 | 415.3 |
| | K ⁺ | 91.34 | 92.47 | 88.28 | 17.32 | 39.96 | 63.4 | 101.7 | 80.83 |
| | Mg ²⁺ | 249.9 | 226.0 | 203.8 | 266.3 | 319.8 | 365.2 | 172.1 | 134.5 |
| | Ca ²⁺ | 1608.4 | 1503.4 | 1330.1 | 1855.0 | 2014.6 | 2125.9 | 1086.2 | 915.5 |
| 7 | Na ⁺ | 591.3 | 696.2 | 600.0 | 289.1 | 514.1 | 279.6 | 552.8 | NA |
| | K ⁺ | 76.85 | 85.99 | 86.91 | 17.28 | 48.05 | 24.47 | 106.3 | |
| | Mg ²⁺ | 240.8 | 286.3 | 173.3 | 267.6 | 327.6 | 358.3 | 175.8 | |
| | Ca ²⁺ | 1641.0 | 2112.4 | 1270.4 | 1831.2 | 2073.4 | 2082.0 | 1165.8 | |
| 8 | Na ⁺ | 346.7 | 672.9 | 594.1 | 292.1 | 536.8 | 263.5 | 531.3 | 408.3 |
| | K ⁺ | 35.67 | 84.26 | 89.15 | 18.48 | 53.02 | 20.3 | 105.7 | 76.95 |
| | Mg ²⁺ | 233.1 | 280.9 | 173.3 | 281.7 | 314.8 | 328.0 | 171.4 | 133.0 |
| | Ca ²⁺ | 1629.4 | 2048.2 | 1227.2 | 1866.1 | 1987.8 | 1940.2 | 1128.2 | 1005.9 |

Appendix V – Cation concentrations in the Hillsborough River (μM) (continued)

| Station # | Cations | 07/24/2000 | 08/22/2000 | 10/04/2000 | 01/30/2001 | 05/02/2001 | 06/25/2001 | 08/27/2001 | 09/13/2001 |
|-----------|------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 9 | Na ⁺ | 352.3 | 646.2 | 591.3 | 234.0 | 556.3 | 247.1 | 516.2 | 401.3 |
| | K ⁺ | 39.59 | 89.65 | 90.09 | 15.10 | 56.03 | 20.9 | 104.5 | 75.23 |
| | Mg ²⁺ | 230.3 | 253.7 | 174.9 | 223.1 | 308.8 | 311.9 | 167.6 | 132.9 |
| | Ca ²⁺ | 1598.1 | 1850.3 | 1241.5 | 1424.4 | 1964.9 | 1839.9 | 1099.9 | 982.0 |
| 10 | Na ⁺ | 1820.6 | 851.9 | 576.6 | 637.2 | 1671.4 | 1108.7 | 439.0 | 289.2 |
| | K ⁺ | 76.59 | 75.27 | 92.06 | 29.17 | 76.39 | 38.13 | 99.39 | 76.43 |
| | Mg ²⁺ | 375.5 | 285.7 | 173 | 342.2 | 424.2 | 393.2 | 148.0 | 127.2 |
| | Ca ²⁺ | 1575.7 | 1733.7 | 1257.9 | 1933.0 | 2055.3 | 1721.6 | 1004.7 | 979.5 |
| 11 | Na ⁺ | 85982 | 44364 | 18011.5 | 516.26 | | | | |
| | K ⁺ | 1903 | 809 | 407.4 | 1713 | NA | NA | NA | NA |
| | Mg ²⁺ | 9771 | 5016 | 1857.6 | 9589 | | | | |
| | Ca ²⁺ | 2786 | 3303 | 2124 | 4301 | | | | |
| 12 | Na ⁺ | 189185 | 66013 | 40190 | 175685 | | | | |
| | K ⁺ | 4043 | 1330 | 748 | 3740 | NA | NA | NA | NA |
| | Mg ²⁺ | 21448 | 7596 | 3491 | 20208 | | | | |
| | Ca ²⁺ | 5073 | 3490 | 1050 | 5966 | | | | |
| 13 | Na ⁺ | 376570 | 260741 | 159167 | 373463 | | | | |
| | K ⁺ | 8104 | 5678 | 3480 | 8199 | NA | NA | NA | NA |
| | Mg ²⁺ | 42782 | 30670 | 17511 | 42846 | | | | |
| | Ca ²⁺ | 8728 | 7152 | 3937 | 9379 | | | | |

Appendix V – Cation concentrations in the Hillsborough River (µM) (continued)

| Station # | Cations | 09/19/2001 | 11/19/2001 |
|-----------|------------------|------------|------------|
| 1 | Na ⁺ | 129.1 | 322.4 |
| | K ⁺ | 75 | 21.9 |
| | Mg ²⁺ | 83.93 | 170.7 |
| | Ca ²⁺ | 556.0 | 1722.1 |
| 2 | Na ⁺ | 321.8 | 2305.7 |
| | K ⁺ | 129.4 | 359.7 |
| | Mg ²⁺ | 141.9 | 326.9 |
| | Ca ²⁺ | 438 | 1461.3 |
| 3 | Na ⁺ | 186.3 | 498.8 |
| | K ⁺ | 82.79 | 50.57 |
| | Mg ²⁺ | 99.2 | 201.5 |
| | Ca ²⁺ | 480.0 | 1593.5 |
| 4 | Na ⁺ | 323.4 | 648.4 |
| | K ⁺ | 94.56 | 68.39 |
| | Mg ²⁺ | 125.0 | 181.2 |
| | Ca ²⁺ | 456.4 | 1226.6 |
| 5 | Na ⁺ | 199.3 | 630.9 |
| | K ⁺ | 79.1 | 70.39 |
| | Mg ²⁺ | 85.2 | 208.9 |
| | Ca ²⁺ | 452.9 | 1515.4 |
| 6 | Na ⁺ | NA | 563.5 |
| | K ⁺ | NA | 61.99 |
| | Mg ²⁺ | NA | 198.7 |
| | Ca ²⁺ | NA | 1438.7 |
| 7 | Na ⁺ | 208.8 | 520.1 |
| | K ⁺ | 72.17 | 64.94 |
| | Mg ²⁺ | 75.06 | 207.1 |
| | Ca ²⁺ | 536.9 | 1481.5 |

Appendix V – Cation concentrations in the Hillsborough River (μM) (continued)

| Station # | Cations | 09/19/2001 | 11/19/2001 |
|-----------|------------------|------------|------------|
| 8 | Na ⁺ | 201.7 | 487.6 |
| | K ⁺ | 69.91 | 58.77 |
| | Mg ²⁺ | 73.59 | 186.9 |
| | Ca ²⁺ | 481.6 | 1317.9 |
| 9 | Na ⁺ | 209.7 | 572.6 |
| | K ⁺ | 71.09 | 68.82 |
| | Mg ²⁺ | 76.1 | 211.8 |
| | Ca ²⁺ | 503.3 | 1486.8 |
| 10 | Na ⁺ | 243.8 | 571.9 |
| | K ⁺ | 79.64 | 74.5 |
| | Mg ²⁺ | 87.08 | 227.9 |
| | Ca ²⁺ | 573.4 | 1512.4 |
| 11 | Na ⁺ | 2147.7 | 74656 |
| | K ⁺ | 99 | 1589 |
| | Mg ²⁺ | 284.8 | 8354 |
| | Ca ²⁺ | 993.8 | 4520 |
| 12 | Na ⁺ | 2756.5 | 85957 |
| | K ⁺ | 102.7 | 1859 |
| | Mg ²⁺ | 345.1 | 9572 |
| | Ca ²⁺ | 984.4 | 4320 |
| 13 | Na ⁺ | 54736 | 219481 |
| | K ⁺ | 1295 | 4667 |
| | Mg ²⁺ | 6537 | 24859 |
| | Ca ²⁺ | 2372 | 6176 |

Appendix VI – Anion concentrations in the Hillsborough River (µM)

| Station # | Anions | 06/20/2000 | 07/24/2000 | 08/22/2000 | 05/02/2001 | 06/25/2001 | 08/27/2001 | 09/13/2001 | 09/19/2001 | 11/19/2001 |
|-----------|-------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 1 | F ⁻ | 12.97 | 17.36 | 18.83 | 12.11 | 3.68 | 11.14 | 10.60 | 6.91 | 11.18 |
| | Cl ⁻ | 281.0 | 269.3 | 281.7 | 324.1 | 294.8 | 291.2 | 185.5 | 131.2 | 310.6 |
| | NO ₃ ⁻ | NA | NA | NA | ND | 9.03 | 27.43 | 9.14 | ND | 15.62 |
| | SO ₄ ²⁻ | 178.7 | 168.7 | 179.4 | 231.9 | 227.2 | 84.63 | 70.75 | 42.05 | 168.2 |
| | CA ^a | 2542.4 | 2997.5 | 3163.5 | 3322.2 | 2984.1 | 2003.0 | 1368.3 | 1239.5 | 3452.2 |
| 2 | F ⁻ | 27.13 | 31.19 | 27.26 | 23.68 | 24.21 | 34.64 | 19.53 | 13.23 | ND |
| | Cl ⁻ | 3976.5 | 1498.3 | 1092.8 | 688.9 | 3533.2 | 1357.8 | 972.7 | 316.0 | 1720.1 |
| | NO ₃ ⁻ | NA | NA | NA | 23.55 | 32.58 | 33.87 | 35.95 | 4.23 | 51.08 |
| | SO ₄ ²⁻ | 1915.6 | 424.2 | 360.6 | 193.5 | 1669.7 | 595.3 | 379.5 | 118.0 | 610.2 |
| | CA ^a | 1893.1 | 2373.5 | 2439.7 | 1942.1 | 2939.0 | 2836.0 | 1930.7 | 1002.1 | 3237.2 |
| 3 | F ⁻ | 9.09 | 79.96 | 20.76 | 7.89 | 4.74 | 13.01 | 13 | 9.91 | 8.5 |
| | Cl ⁻ | 303.3 | 567.7 | 563.4 | 332.9 | 608.7 | 496.7 | 365.6 | 197.3 | 445.0 |
| | NO ₃ ⁻ | NA | NA | NA | 112.6 | 99.35 | 67.96 | 32.88 | 7.28 | 98.74 |
| | SO ₄ ²⁻ | 105.5 | 256.8 | 219.6 | 127.0 | 257.7 | 214.7 | 144.8 | 66.8 | 174.9 |
| | CA ^a | 2640.4 | 2970.8 | 3091.6 | 3491.7 | 3142.0 | 2690.8 | 1891.3 | 1053.6 | 3233.5 |
| 4 | F ⁻ | 8.82 | 78.69 | 20.86 | 7.89 | 2.63 | 17.67 | 16.53 | 15.03 | 11.75 |
| | Cl ⁻ | 303.7 | 528.4 | 666.6 | 373.2 | 586.2 | 537.2 | 534.4 | 359.3 | 678.7 |
| | NO ₃ ⁻ | NA | NA | NA | 72.90 | 74.19 | 24.45 | 0 | 0 | 55.16 |
| | SO ₄ ²⁻ | 109.5 | 358.9 | 753.9 | 155.8 | 261.0 | 174.8 | 165.3 | 126.5 | 208.4 |
| | CA ^a | 2809.6 | 2875.1 | 2617.2 | 3530.1 | 3218.5 | 2363.0 | 1560.8 | 936.9 | 2362.9 |

Appendix VI – Anion concentrations in the Hillsborough River (µM) (continued)

| Station # | Anions | 06/20/2000 | 07/24/2000 | 08/22/2000 | 05/02/2001 | 06/25/2001 | 08/27/2001 | 09/13/2001 | 09/19/2001 | 11/19/2001 |
|-----------|-------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 5 | F ⁻ | 9.54 | 79.38 | 21.92 | 12.11 | 2.63 | 20.48 | 17.15 | 12.71 | 11.65 |
| | Cl ⁻ | 300.8 | 573.6 | 630.2 | 414.7 | 633.6 | 545.3 | 443.3 | 196.1 | 556.8 |
| | NO ₃ ⁻ | NA | NA | NA | 62.10 | 65.00 | 17.5 | 8.71 | 0 | 52.3 |
| | SO ₄ ²⁻ | 109.6 | 243.5 | 990.2 | 172.0 | 278.4 | 145 | 140.7 | 75.23 | 201 |
| | CA ^a | 2903.1 | 2845.4 | 2624.7 | 3469.8 | 3149.7 | 2344.8 | 2075.5 | 974.0 | 3119.6 |
| 6 | F ⁻ | 10.06 | 80.36 | 19.23 | 8.42 | 7.37 | 17.91 | 4.59 | NA | 12.44 |
| | Cl ⁻ | 278.8 | 605.9 | 565.9 | 390.4 | 485.5 | 535.5 | 137.6 | NA | 544.8 |
| | NO ₃ ⁻ | NA | NA | NA | 60.97 | 33.06 | 8.10 | 0.00 | NA | 37.68 |
| | SO ₄ ²⁻ | 345.9 | 522.6 | 784.1 | 167.1 | 1001.6 | 144.0 | 41.70 | NA | 225.6 |
| | CA ^a | 2322.5 | 2803.2 | 2039.1 | 4359.1 | 3031.6 | 2281.6 | 2358.3 | NA | 2846.5 |
| 7 | F ⁻ | 10.32 | 79.42 | 20.43 | 10.53 | 57.89 | 20.06 | NA | 9.65 | 12.15 |
| | Cl ⁻ | 280.1 | 527.9 | 598.3 | 434.4 | 322.4 | 527.5 | NA | 232.5 | 516.4 |
| | NO ₃ ⁻ | NA | NA | NA | 24.52 | 24.84 | ND | NA | ND | 21.32 |
| | SO ₄ ²⁻ | 326.1 | 625.5 | 1512.4 | 772.4 | 938.8 | 140.2 | NA | 69.54 | 198.6 |
| | CA ^a | 2264.7 | 2562.9 | 1925.5 | 3346.6 | 2897.9 | 2494.9 | NA | 1115.5 | 550.6 |
| 8 | F ⁻ | 10.41 | 78.67 | 20.69 | 10.53 | 49.47 | 27.8 | 11.74 | 9.57 | 12.48 |
| | Cl ⁻ | 278.4 | 384.2 | 616.3 | 453.6 | 306.9 | 514.6 | 404.4 | 215.6 | 516.3 |
| | NO ₃ ⁻ | NA | NA | NA | 18.87 | 29.84 | ND | ND | ND | 23.22 |
| | SO ₄ ²⁻ | 349.5 | 520.4 | 1568.2 | 675.1 | 878.1 | 138.0 | 133.8 | 67.22 | 224.4 |
| | CA ^a | 2295.8 | 2590.8 | 1629.1 | 3357.3 | 2674.7 | 2397.7 | 2068.7 | 1010.3 | 374.2 |
| 9 | F ⁻ | 10.41 | 77.98 | 19.8 | 10.53 | 16.32 | 16.95 | 11.65 | 9.6 | 12.19 |
| | Cl ⁻ | 285.7 | 392.2 | 596.4 | 476.5 | 289.1 | 502.7 | 401 | 219.4 | 492.9 |
| | NO ₃ ⁻ | NA | NA | NA | 0.00 | 24.68 | ND | ND | ND | 21.58 |
| | SO ₄ ²⁻ | 305.5 | 618.1 | 1321.9 | 678.5 | 816.2 | 137.5 | 134.0 | 68.91 | 213.5 |
| | CA ^a | 2391.0 | 2327.9 | 1669.5 | 3312.0 | 2604.3 | 2339.2 | 2014.9 | 1060.2 | 841.9 |

Appendix VI – Anion concentrations in the Hillsborough River (μM) (continued)

| Station # | Anions | 06/20/2000 | 07/24/2000 | 08/22/2000 | 05/02/2001 | 06/25/2001 | 08/27/2001 | 09/13/2001 | 09/19/2001 | 11/19/2001 |
|-----------|-------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 10 | F ⁻ | 11.69 | 80.34 | 22.1 | 13.16 | 12.63 | 14.37 | 10.9 | 11.94 | 12.8 |
| | Cl ⁻ | 3282.2 | 2163.3 | 864.3 | 1929.5 | 1348.7 | 412.7 | 389.2 | 236.8 | 554.0 |
| | NO ₃ ⁻ | NA | NA | NA | 0.00 | 0.00 | 0 | 0 | 0 | 0 |
| | SO ₄ ²⁻ | 775.1 | 783.0 | 1083.2 | 997.1 | 943.7 | 140.9 | 156.2 | 93.91 | 316.7 |
| | CA ^a | 1298.1 | 1984.5 | 1907.7 | 2767.0 | 2126.3 | 2113.3 | 1860.1 | 1194.8 | 2921.6 |
| 11 | F ⁻ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | Cl ⁻ | NA | 129064 | 41738 | NA | NA | NA | NA | 2291.8 | 83979 |
| | NO ₃ ⁻ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | SO ₄ ²⁻ | NA | 7276 | 3860 | NA | NA | NA | NA | 287.3 | 6140 |
| 12 | F ⁻ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | Cl ⁻ | 214600 | 239341 | 63324 | NA | NA | NA | NA | 3400.8 | 103700 |
| | NO ₃ ⁻ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | SO ₄ ²⁻ | 10909 | 11946 | 4733 | NA | NA | NA | NA | 388.7 | 6748 |
| 13 | F ⁻ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | Cl ⁻ | 345024 | 468696 | 296577 | NA | NA | NA | NA | 47393 | 332839 |
| | NO ₃ ⁻ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | SO ₄ ²⁻ | 16044 | 21563 | 14405 | NA | NA | NA | NA | 2460 | 16058 |

^a CA (carbonate alkalinity) is calculated from charge balance ($\text{CA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$), and at typical river pH $[\text{HCO}_3^-] \gg [\text{CO}_3^{2-}]$.

^b CA not calculated for Stations 11-13. Since CA is a minor constituent in seawater, it cannot be calculated for Stations 11-13 which exhibit seawater like characteristics.

Appendix VII – ΣPO₄ concentrations in the Hillsborough River (μM)

| Station # | 09/19/1999 | 10/23/1999 | 11/21/1999 | 12/20/1999 | 01/20/2000 | 02/21/2000 | 03/20/2000 | 04/17/2000 | 05/22/2000 | 06/20/2000 |
|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 1 | 1.63 | 3.48 | 1.22 | 1.55 | 0.81 | 3.67 | 2.12 | 2.06 | 2.12 | 2.87 |
| 2 | 13.40 | 14.00 | 9.11 | 10.78 | 11.70 | 11.11 | 15.53 | 13.07 | 15.45 | 13.66 |
| 3 | 4.16 | 4.62 | 2.50 | 4.77 | 1.77 | 2.04 | 2.19 | 3.52 | 1.57 | 2.12 |
| 4 | 6.04 | 5.45 | 3.30 | 3.00 | 2.21 | 3.12 | 2.65 | 1.95 | 1.75 | 1.76 |
| 5 | 6.32 | 5.97 | 3.77 | 3.34 | 2.50 | 3.07 | 2.96 | 2.26 | 2.21 | 1.86 |
| 6 | 5.18 | 6.19 | 3.69 | 3.60 | 2.65 | 3.07 | 2.86 | 2.15 | 0.27 | 1.52 |
| 7 | 4.80 | 6.40 | 3.34 | 2.87 | 2.64 | 2.66 | 2.58 | 1.24 | 0.16 | 0.75 |
| 8 | 5.14 | 6.84 | 3.57 | 2.89 | 2.55 | 2.46 | 2.54 | 1.37 | 0.86 | 0.96 |
| 9 | 5.65 | 6.71 | 3.91 | 2.86 | 2.72 | 2.27 | 2.46 | 1.73 | 2.71 | 1.70 |
| 10 | 5.73 | 6.06 | 0.21 | 1.25 | 0.59 | 0.07 | 1.21 | 1.53 | 2.05 | 1.12 |
| 11 | 3.83 | 4.75 | 3.57 | 3.99 | 3.18 | 3.34 | 6.91 | 5.38 | 6.67 | 8.80 |
| 12 | 4.55 | 5.35 | 3.87 | 4.40 | 2.84 | 3.10 | 7.49 | 5.25 | 8.65 | 8.55 |
| 13 | 6.42 | 6.40 | 4.22 | 4.47 | 3.33 | 4.03 | 5.66 | 4.55 | 5.43 | 7.05 |

Appendix VII – ΣPO₄ concentrations in the Hillsborough River (μM) (continued)

| Station # | 07/24/2000 | 08/22/2000 | 10/04/2000 | 01/30/2001 | 05/02/2001 | 06/25/2001 | 08/27/2001 | 08/30/2001 | 09/04/2001 | 09/08/2001 |
|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 1 | 3.17 | 3.24 | 1.90 | 1.70 | 1.87 | 2.05 | 14.25 | 16.49 | 12.77 | 10.65 |
| 2 | 18.97 | 14.04 | 13.10 | 10.99 | 14.59 | 9.53 | 15.04 | 18.88 | 14.70 | 12.55 |
| 3 | 7.69 | 9.86 | 6.52 | 0.80 | 2.13 | 4.07 | 10.60 | 8.16 | 5.97 | 10.83 |
| 4 | 4.34 | 10.48 | 8.43 | 0.91 | 2.67 | 2.65 | 13.16 | 11.94 | 9.72 | 8.53 |
| 5 | 5.03 | 10.00 | 9.31 | 0.94 | 2.90 | 3.11 | 14.20 | 14.33 | 11.21 | 10.47 |
| 6 | 5.24 | 6.77 | 9.46 | 1.04 | 2.34 | 2.65 | 14.20 | 14.47 | 11.77 | 4.45 |
| 7 | 4.77 | 7.11 | 7.40 | 0.62 | 2.23 | 2.65 | 12.91 | 13.38 | 11.65 | 6.02 |
| 8 | 3.08 | 8.59 | 8.00 | 0.40 | 2.84 | 2.10 | 13.57 | 14.91 | 12.44 | 7.18 |
| 9 | 3.42 | 9.67 | 8.41 | 0.37 | 2.51 | 3.26 | 14.52 | 14.74 | 13.11 | 8.18 |
| 10 | 1.89 | 3.67 | 7.36 | 0.04 | 1.91 | 0.90 | 14.43 | 15.41 | 12.77 | 12.18 |
| 11 | 5.72 | 4.70 | 4.83 | 3.31 | NA | NA | NA | NA | NA | NA |
| 12 | 7.80 | 4.62 | 6.24 | 4.25 | NA | NA | NA | NA | NA | NA |
| 13 | 8.32 | 5.83 | 6.67 | 3.28 | NA | NA | NA | NA | NA | NA |

Appendix VII – ΣPO_4 concentrations in the Hillsborough River (μM) (continued)

| Station # | 09/13/2001 | 09/19/2001 | 11/19/2001 |
|-----------|------------|------------|------------|
| 1 | 9.73 | 14.84 | 2.63 |
| 2 | 17.96 | 26.28 | 8.71 |
| 3 | 12.84 | 17.31 | 2.61 |
| 4 | 12.94 | 11.02 | 4.89 |
| 5 | 13.40 | 14.19 | 4.94 |
| 6 | 8.12 | NA | 5.22 |
| 7 | NA | 5.51 | 4.92 |
| 8 | 7.03 | 7.99 | 4.58 |
| 9 | 7.13 | 8.36 | 4.57 |
| 10 | 7.14 | 8.77 | 3.60 |
| 11 | NA | 6.17 | 4.55 |
| 12 | NA | 5.06 | 4.41 |
| 13 | NA | 4.77 | 4.50 |

Appendix VIII – Calculated Ω (Saturation State) Values (as log Ω)

| Station # | 05/22/2001 | 06/25/2001 | 08/27/2001 | 09/19/2001 | 11/19/2001 |
|-----------|------------|------------|------------|------------|------------|
| 1 | 0.148 | 0.159 | -0.724 | -1.425 | 0.084 |
| 2 | -0.392 | 0.333 | -0.188 | -1.682 | 0.034 |
| 3 | 0.671 | 0.450 | -0.155 | -1.394 | 0.292 |
| 4 | 0.848 | 0.644 | -0.774 | -1.749 | -0.314 |
| 5 | 0.855 | 0.586 | -0.790 | -1.941 | -0.015 |
| 6 | 0.945 | 0.543 | -0.835 | NA | -0.115 |
| 7 | 0.733 | 0.483 | -0.873 | -1.644 | -0.748 |
| 8 | 0.668 | 0.431 | -0.859 | -1.714 | NA |
| 9 | 0.706 | 0.287 | -0.873 | -1.632 | -0.604 |
| 10 | 0.461 | 0.938 | -0.649 | -1.344 | 0.444 |