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# Quantifying Anthropogenic Indicators and Changes in Dissolved Organic Matter in Coastal Urban Aquatic Ecosystems Exposed to High Tidal Flooding

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#### FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

## QUANTIFYING ANTHROPOGENIC INDICATORS AND CHANGES IN DISSOLVED ORGANIC MATTER IN COASTAL URBAN AQUATIC ECOSYSTEMS EXPOSED TO HIGH TIDAL FLOODING

An Undergraduate Honors Thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science

in

### BIOLOGICAL SCIENCES

#### WITH HONORS

by

Gonzalo Eyzaguirre

#### Dr. Steven Oberbauer, Chairperson Department of Biological Sciences To:

This Undergraduate Honors Thesis in Biological Sciences, written by Gonzalo Eyzaguirre entitled "Quantifying Anthropogenic Indicators and Changes in Dissolved Organic Matter in Coastal Urban Aquatic Ecosystems Exposed to High Tidal Flooding", is submitted to you in partial fulfillment of the requirements for Undergraduate Honors in Biological Sciences. The Biological Sciences Undergraduate Honors Committee and the candidate's research supervisor have read this thesis. We recommend that it be approved,

**Dr.** John Kominoski Honors Research Supervisor

Walter M. Goldberg

Dr. Walter M. Goldberg, Chairperson, Undergraduate Honors Committee

Date of Honors Research Presentation: April 15, 2019 This thesis by Gonzalo Eyzaguirre is approved.

 $2$  able

Dr. Steven Oberbauer, Chairperson Department of Biological Sciences

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#### **ABSTRACT**

Sea-level rise is causing an increase in tidal flooding in coastal urban areas. Extreme high tides, also known as king tides, are peak tide moments in which tidal amplitude is increased and shallow groundwater flows from the underlying water table are introduced. During tidal flooding in urban areas, accumulated anthropogenic indicators of different water sources are released from groundwater to surface waters, but how these tidal events affect the contributions of different water sources to urban flood waters is uncertain. We quantified tracers of anthropogenic origin including fluoride, fecal coliform bacteria, as well as dissolved organic carbon (DOC) concentrations and dissolved organic matter (DOM) composition from inflowing and outflowing waters of Wagner Creek and the Coral Gables waterway (Miami, Florida, USA) during a king tide event. We measured higher DOC and fluoride concentrations at downstream coastal sites of both transects that decreased upstream, and during tidal flooding concentrations of both were highest in fall tide waters compared to rising and peak tides. Tidal flooding increased anthropogenic indicators (fecal coliform and fluoride) in urban surface waters, and we measured higher levels of both in Coral Gables waterway than in Wagner Creek. Biological Index values associated with DOM were higher upstream in Wagner Creek and downstream in Coral Gables waterway. Tidal influence and proximity to the coast were important determinants in our ability to detect municipal and wastewater indicators. Extreme high tide events pose threats to low-lying communities as increasing sea level rise will lead to prominent concentrations of anthropogenic signatures causing environmental stress and imminent threats to public health as groundwater inundation continues to pollute surface waters.

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#### **INTRODUCTION**

Cities manifest unique ecological and sociologic features that drive environmental change at multiple scales (Grimm et al. 2008). Human activities have transformed natural ecosystems, but how these modified and engineered systems function is largely uncertain (Hale et al. 2015). Management of storm water is a primary feature of many urban municipalities, and the complexity of cities – including their infrastructure, geology, geographic location, and climate – as well as how humans modify and manage water within can influence the dynamics of flooding and associated water quality (Hale et al. 2015).

Coastal urban ecosystems are exposed to flooding from both marine and terrestrial sources. Sea level rise, for example, poses an incremental risk due to thermal expansion of water as Earth's temperature increases due to changes in global climate. The Intergovernmental Panel on Climate Change has concluded that global mean sea level will rise by 1 m or more throughout the 21<sup>st</sup> century due to concentration of various greenhouse gases in the environment. (Nicholls, 2004). The marginal rise in sea level causes changes in the depth of coastal urban waterways, resulting in overflow of surface water and flooding. Lowland coastal communities are also more susceptible to tidal variation, as they result in sunny-day flooding due to elevation in the water table from rainfall and saltwater intrusion. Inland groundwater rises due to increases in sea level can produce additional sources of inland inundation that can also pose threats to urban communities that are increasing dramatically as population levels rise (Habel, 2017). Among the Earth's population, about 700 million people live in low-lying coastal areas, and this number continues to rise as coastal migration expands (McGranahan et al. 2007)

Flooding in coastal urban areas is influenced by freshwater runoff, groundwater levels, and tidal flood events. Floods account for approximately 40% of all natural disasters and affect 20-300 million people every year. (Dewan 2013). As coastal groundwaters reside at or above sea

level, the fluctuations between groundwater and ocean oscillations are closely correlated, meaning that groundwater tables increase by a similar magnitude as sea level rises. (Habel et al. 2017). Tides of especially high amplitudes, 'king tides', have been increasingly studied due to their contributions to inland flooding. These tides occur when the Earth and moon, as well as the Earth and Sun become most closely aligned in their annual orbits, combining their gravitational forces to create tides of notable heights. Because king tides add amplitude to mean high sea levels they pose local flood risks to low-lying coastal comminutes that can be damaging to urban socioeconomics and infrastructure. (Wdowinski et al. 2016).

Although global sea level rise is a serious problem, flooding hazards are unique for each coastal community, where flooding risk is based on local elevation and regional sea level rise (Sukop et al. 2001). In south Florida the average rate of sea level rise has become amplified exponentially, increasing from  $3 \pm 2$  mm/yr prior to 2006 to  $9 \pm 4$  mm/yr after 2006 (Wdowinski et al. 2016) The intensity of this flooding can escalate with increasing levels of local rainfall, storm surge, and tides (Aerts et al. 2014). Throughout the USA, chronic inundation is becoming a burden of everyday life. In Miami Beach, traffic must be rerouted and local businesses are suffering large losses in revenue due to tidal flooding (Veiga, 2014). Coastal neighborhoods can also be isolated when floodwaters rise and block main streets, leaving residents without access to inland facilities (Wdowinski et al. 2016). Damage due to flooding hinges largely on the vertical extent of unsaturated space between tidally influenced tidal groundwater and infrastructure such as septic tanks, sewage treatment facilities, and municipal pipes. (Habel et al. 2017). The narrowing of this space not only leads to destruction of previously built infrastructure and property values; it can also affect the water quality of these floodwaters (McAlpine and Porter, 2018.

During urban flooding when shallow groundwater is elevated, anthropogenic material from waste and municipal water sources may leak into urban rivers and canals. Floodwaters can also infiltrate the sanitary sewage collection and cause overflows or overloading of these systems, resulting in the infiltration of harmful contaminants in bays, rivers, canals, and the ocean. King tides pose an additional threat to urban aquatic ecosystems by elevating groundwater levels and increasing the likelihood of contaminant release into storm water and nearby aquatic ecosystems. Anthropogenic tracers, such as fluoride, sucralose (Batchu et al. 2015, Sankararamakrishnan and Guo 2005, Hibbs and Boghici, 1999) and fecal coliform may be indicators of sewage or municipal water leaks that can affect water quality in urban water ways (Dewan, 2013). The use of tracers to isolate different municipal and waste water sources is important to managing groundwater and surface water quality as well as understanding their relative contributions to urban flood waters.

The objective of this research is to test the effects of tidal flooding on the relative contribution of municipal and waste water sources to urban flood waters. This study will examine the effect of high-tide events on water source and quality in rivers and canals in Miami, FL, where the following relationships will be tested: (i) do tidal flooding events affect the concentrations of dissolved organic carbon in urban rivers and canals and (ii) do flood events influence the amount of municipal and waste water tracers in fluvial systems.

The high population density, flat topography, and subtropical climate of south Florida and Miami in particular, make this region especially vulnerable to flooding from runoff and sea level rise (Wanless and Vlaswinkel 2005; Melillo 2014). Several studies have used coastal community population, elevation, and infrastructure to predict possible hazards of coastal flooding (e.g., Adelekan 2010; Spanger-Siegfried et al 2014). However, to my knowledge, there is no study that evaluates the effect of king tides on groundwater intrusion/inundation in coastal

waterways. This study aims to quantify the changes in anthropogenic contaminants including fecal coliform and fluoride before, during, and after these events. Fluorescence and dissolved organic carbon will be analyzed in these waterways to give insight into runoff sources and watershed distribution (Singh et al. 2019; Inamdar et. al 2013).

#### **MATERIALS AND METHODS**

#### *Study area*

South Florida and other coastal regions have man-made waterways that drain low-lying lands for domestic and agricultural development in urban ecosystems (Irlandi et al. 1997). This study occurred in two different waterways in Miami-Dade County, Florida that represent such urbanized, low-lying areas. Upstream to downstream transects were established within the Coral Gables Canal and Wagner Creek. The Coral Gables canal redirects natural surface flow, periodically releasing fresh water into coastal bays and receiving saltwater contributions during high tide. Wagner Creek is a 2.6-km tributary of the Miami River that drains out of the Biscayne Aquifer into what used to be the Allapattah prairie -as it runs through the urbanized neighborhoods of Miami (Al-Amin et al. 2013; Goodwin et al. 2009).

To identify municipal and wastewater contributions to these waterways, surface water samples were collected along transects in both Wagner Creek and Coral Gables Canal (Figure 1). The Coral Gables sampling sites included two locations: Blue Road (CGBR), and Cocoplum (CGCP). The CGBR site is inland in comparison with GCCP, which is coastal and drains into Biscayne Bay. In Figure 1, the Wagner Creek sampling sites are shown including WC01 (N) the most downstream transect right at divergence point from the Miami River, as well as the WC02 and WC03 sites, which are intermediaries. The WC04 site is located most inland.



**Figure 1:** Wagner Creek tributary and Coral Gables waterway sites in Miami, Fl are shown with named transects. The Wagner Creek tributary is shown above with transect points numbered from downstream to upstream (WC01, WC02, WC03, WC04). The Coral Gables waterway is shown with transect points running from downstream (CGCP) to upstream (CGBR).

#### *Sample Collection*

To distinguish extreme high tide events, the NOAA tide tables at the Government Cut location were used to examine the days with highest tidal amplitudes. In coordination with FIU Sea Level Solutions Day, October 27, 2018 was chosen for sampling due to significant tidal amplitude reaching 1.15m (NOAA, 2018). Three sample times were established to correspond with the timing of rising tide (10:00 am), peak tide (11:00 am), and falling tide (12:00 pm). Samples were also collected on August 2018 and December 2018 to compare the effect of these extreme high tides with other high tides that occur throughout the wet season. Samples were collected along transects throughout Wagner Creek tributary and Coral Gables waterway. (Figure 1)

Samples were collected by filling sterile 50 mL amber bottles with surface water, followed by immediate filtration through a 0.45 μm Millipore filter. These samples were then refrigerated until analyzed to quantify the concentration of dissolved organic carbon (DOC), fluoride, and fluorescence. Fecal coliform data collected monthly at downstream transects were used to evaluate possible relationships between transect location and wastewater leaks.

#### *Fluoride Concentration*

The concentration of fluoride in these surface water samples was measured using a Dionex Aquion Ion Chromatography (IC) System that separates inorganic anions based on their affinity to the Dionex IonPac AS22 (4X250 mm alkanol quaternary ammonium) ion exchanger. Standards were made to measure baseline fluoride concentration were made with DI water ranging from fluoride concentrations of 0.1 to 1.5 ppm and were used to compare peaks at the same position on the ion chromatograph output. The standard peak heights created a linear calibration curve (r=.9999) that was used to calculate the concentration of fluoride in the samples following the procedure of Lou et al. 2017.

#### *Fluorescence and EEM analysis*

Dissolved organic matter processing utilized the approaches of Guo et al. (2011) and Stedmon et al. (2005). The fluorescent properties of surface-water samples were analyzed using an AquaLog benchtop fluorometer. This instrument is able to produce a 3D scan, resulting in a contour plot of excitation wavelength and emission wavelength as a function of fluorescence intensity, called an excitation emission matrix (EEM). These EEMs were calculated using an excitation wavelength range of 240-455 with and an emission range of  $\lambda$ ex + 10 nm to  $\lambda$ ex + 250 nm with in a 1cm quartz cuvette (Lopez et al. 2005). The excitation slit width was set to 5.7 nm and the emission spectra was set to 2nm. The fluorescence scan was collected with an integration time of 0.25 sec due to its optical properties (Yamashita et al. 2013). Fluorescence indices included, HIX, BIX, FI calculated using Matlab version xs to derive peak intensities across fluorescent spectra. The humification index (HIX) corresponds to the level of terrestrial derived dissolved organic matter (DOM) components that are typically aromatic. The biological index (BIX) corresponds to the level of recently produced DOM often coincides with the amount of algal or protein like components. The fluorescence index (FI) indicates marine-derived sources of DOM (Stedmon et al. 2005).

#### *DOC and Fecal Coliform*

Dissolved organic carbon was measured November 2018 at the Southeast Environmental Research Center's water quality lab at Florida International University with a Shimadzu TOC-V CSH TOC analyzer using the high temperature combustion method of Cooper (2016). Samples of fecal coliform were taken from surface waters monthly throughout the year by the Miami-Dade County Department of Environmental Resource Management. Samples were first filtered through a 0.45 μm sterile membrane filter. The membrane was then placed on a selective

medium (mFC), incubated at 44.5°C submerged in a water bath, and presumptive fecal coliform colonies were enumerated. These presumptive fecal coliform colonies were then screened to verify fecal-specific origin. Confirmed colonies were counted and reported using colony forming units (CFU) in 100 mL of sample (Liu and Huang, 2012).

#### **RESULTS**

#### *High Tide Event Tracers: Fluoride and DOC Concentration*

From the surface water samples, one can see the variability in fluoride and DOC concentration between the shifts in rising, peak, and falling tide. The concentrations of fluoride in Figure 2 a and b tend to decrease when shifting from rising tide to peak tide, then increases significantly at falling tide. For example, in Figure 2a station WC02 has an initial fluoride concentration of 0.561 ppm during rising tide. After, it decreases to 0.542 ppm at peak tide and then increases to 0.592 ppm at falling tide. There is also a decreasing concentration of fluoride as you move upstream. Concentrations of DOC have a similar trend in which they decrease throughout the upstream transects, increasing toward the mouth. This suggests flushing of these waterways at the downstream transect.

These trends are further analyzed to produce boxplots comparing the average concentrations of both DOC and fluoride throughout the extreme high tide event in upstream and downstream transects of each waterway. Fluoride and DOC concentrations are significantly higher in downstream transects when compared with upstream locations (Figures 3a, b, c, d), with a p value <0.01 in each section. The concentrations of DOC also show larger variability at downstream ends, indicating a large fluctuation of organic material where tidal influence is greatest (Figure 3c, d).



**Figure 2**: Surface-water tracer concentrations of fluoride and DOC throughout an extreme high tide event occurring on 10/27/18, where rising tide, peak tide, and falling tide are presented for each transect. Fluoride concentrations are shown for Wagner Creek (Figure 3a), and Coral Gables (Figure 3b). The concentrations of DOC are shown for Wagner Creek (Figure 3c) and Coral Gables (Figure 3d). Error bars represent the standard deviation of triplicate samples.



**Figure 3**: Averaged tracer concentrations in upstream and downstream waterway transects. 3a and b: Fluoride concentrations for Wagner Creek, and Coral Gables, respectively. 3c and d: DOC concentrations for transects in Wagner and Coral Gables, respectively. Error bars represent 95% confidence intervals above and below the mean of triplicate samples. Kruskal Chi Squared test determined  $\chi^2$  and p values.

#### *High Tide Event Tracers: Fluorescence Analysis*

From the surface water samples collected on 'king tide' (10/27/18), excitation emission matrices were analyzed to produce HIX, BIX, and FI values (Figure 4). The HIX values correspond to recalcitrant organic matter, showing higher average values downstream in Wagner Creek while

in Coral Gables downstream values were lower (Figure 5a and b). There is more variability in HIX values at downstream transects at those locations, although not significantly so. There is a significant difference in BIX values that represent newly formed organic matter in both Wagner Creek and Coral Gables. Wagner Creek tributary (Figure 3c) has a p value of 0.049 indicating significant differences between elevated values upstream compared with downstream (Figure 4c). Contradictory values are present in Figure 3d, showing that downstream values in Coral Gables are significantly higher compared with upstream with a p value of 0.046. The FI values indicate higher levels upstream in both waterways shown in Figure 3e and f.



10/27/18. Figures represent the upstream and downstream transects in Wagner Creek tributary (4 a, c, e) and Coral Gables waterway (4 b, d, f). Error bars represent 95% confidence intervals above and below the mean. Kruskal Chi Squared test values are shown as  $\chi^2$  and p value.

#### *Seasonal Tracers: Fluoride*

The fluoride concentrations of surface water samples were determined before these king tide events August, as well as during October, and after December. Low concentrations, preliminarily reading 0.211 ppm, were seen during August in WC01, (Figure 5a). In October there is a sharp increase in fluoride concentration at WC01 reaching 0.538 ppm. All other transects showed similar increases in concentration during that month (Figure 5a). December samples show a slight decrease in concentration, maintaining a higher concentration of 0.5 ppm when compared with August values. All transects in Figures 5a and b follow the same trend in which fluoride concentration sharply increases during October, then become slightly reduced in December, however those fluoride values are still higher than in August. Coral Gables also has higher concentrations of fluoride at downstream CGCP throughout the wet season; site WC01 has comparatively reduced concentrations (Figure 5a and b).



**Figure 5**: Surface water fluoride (ppm) concentrations throughout the wet season August-December, compared with Wagner Creek tributary transects shown in Figure 5a, and Coral

Gables waterway transects shown in 5b. Error bars represent standard deviation of the mean (n= 3).

#### *Seasonal Tracers: Downstream Fecal Coliform and Fluoride*

Tracing fecal coliform and fluoride concentrations at the downstream ends where these waterways flush, gives insight to proposed sources of municipal and wastewater leaks. Fluoride and fecal coliform were measured in surface water before extreme high tides in August, during extreme high tides in October, and after these tides in December. Averages of these three months are shown for downstream transects of Wagner Creek tributary and the Coral Gables waterway (Figure 6); the data from Figure 6a has a p value of 0.049 indicating a significant difference between Coral Gables and Wagner Creek fluoride levels. Coral Gables samples retain higher amounts of fluoride throughout the wet season in comparison with Wagner Creek. Although Figure 6b has an insignificant p value of 0.75, Coral Gables expresses marginally higher fecal coliform averages with greater variance.



Figure 6: Downstream surface water fluoride (6a) and fecal coliform average concentrations throughout the wet season August-December (6b). Error bars represent standard deviation (n= 3).

#### **DISCUSSION**

This study illustrates the impact of extreme high tides and how they affect the concentrations of anthropogenic and organic tracers in coastal waterways. There are many natural and anthropogenic ecological sources of groundwater contamination including deep percolation from intensively cultivated fields, liquid and solid wastes from industries, aging municipal pipes, and sewage disposal. (Oren et al. 2004; Chofqi et al., 2004). Fluctuations in anthropogenic contaminants of groundwater are the result of king tides that force these pollutants to the surface (Li et al. 2016, Pitt et al. 1999).

Concentrations of fluoride and DOC seem to be directly correlated. Results confirm that throughout extreme high tide events, anthropogenic contaminants such as fluoride and fecal coliform are released into surface waters at higher concentrations due to the inundation of groundwater. Peak tide showed lowest concentrations of fluoride due to marine water diluting freshwater contributions (Broshears et al. 1993). The release of pressure caused by receding tides allowed contaminants released from groundwater to rise to surface waters, causing there to be highest concentrations throughout falling tide (Zhou et al. 2019). This highlights the process of groundwater subsurface infiltration due to king tides in a short-term data set.

Tidal effects also play a large role in affecting the nearshore groundwater flow and conveyance of dissolved organic matter (DOM). Once relative abundances of DOM were determined using DOC concentrations, fluorescence analysis was able to characterize the spatial variability of DOM source and composition (Jaffé et al. 2004). Although fluorescence indices such as HIX, BIX, and FI have been used to characterize the origin of DOC in environmental areas, the sources, transport, and transformation of DOM are not well understood, especially in urban waterways (Yang et al. 2015).

Due to its active biogeochemical properties, DOM is one of the most substantial geochemical factors controlling the movement of pollutants (Jiang et al. 2018). Coral Gables and Wagner Creek have differing connectivity to the ocean; where Coral Gables Canal drains straight into Biscayne Bay, however, Wagner Creek is a tributary that drains into the tidally influenced Miami River. High variability of HIX values were seen at the downstream ends of both Wagner Creek during king tides, indicating fluctuations of terrestrially derived DOM being imported and exported from the systems. This indicates downstream flushing of large recalcitrant DOM, likely originating from groundwater in Wagner Creek. Coral Gables, being a suburbanized green area; likely receives this increased terrestrial signal from leaf litter from coastal vegetation (Cawley et al. 2014).

Results indicate that these waterways have conflicting flows of recently produced organic matter show by the BIX values. Significantly higher BIX values  $(P<0.01)$  at the downstream end of Coral Gables Canal shows a shift from allochthonous to autochthonous production of DOM, indicating flushing of agricultural and/or urban pollution sources, since this kind of fluorescence has been reported to be enhanced by discharges of untreated sewage and wastewater effluents (Yao et al. 2011). Wagner Creek experienced high BIX values upstream indicating the retainment of pollutants inland. Conceivably due to its industrial environment, having higher sources of inland pollution from residential and industrial runoff (Mostofa et al. 2010).

Marine influence was measured using the FI index that indicates protein-like fluorescence, usually derived from algal and phytoplankton sources (Cawley et al. 2014). Although downstream transects are closer to the coast, FI values at upstream exceed downstream values in both waterways. This indicates that incoming tidal waters are mixing upstream and have an increased residence time before being exported out of the system (Hounshell et al.

2017). Higher variability at the downstream transect of Coral Gables indicates this protein-like DOM is likely due to flushing by tidal oscillations at the coast of Biscayne Bay.

The National Weather Service in Miami, Florida announced that the 2018 wet season would span from May to October due to the sub-tropical climate (NOAA and NWS, 2018). Seasonal results showed a dramatic increase in fluoride concentration in late October, which coincides with the time periods of local king tides and Florida's wet season (Sukop et al. 2001). The increase in this municipal and wastewater tracer does not diminish since in December there were still high levels of fluoride present in surface water. The source is possibly from continuous groundwater intrusion or runoff from elevated precipitation (Poudel, 2016). Maintenance of these high fluoride levels in Coral Gables waterway and Wagner Creek throughout the wet season can pose risks as water tables continue to become uplifted, sea levels continue to rise, and tidal amplitudes increase. High levels of municipal and wastewater in these waterways may pose risks of contamination not only to the local biota but to its residents as a potential source of infection from vector-borne and infectious enteric disease. (De Man et al. 2014, Andrade et al. 2018).

When comparing both waterways, results note higher average levels of both fluoride and fecal coliform bacteria in downstream transects of Coral Gables. Although Coral Gables is a suburbanized sector of Miami, tidal influence at the coast of Biscayne Bay may drive higher levels of contamination in Coral Gables waterway. Wagner creek being a tributary of the Miami River does not receive direct tidal influence; however, spikes in fecal coliform are due to problems in upstream water management. Paul JH et al. describes how wastewater disposal systems currently in widespread use in the Florida Keys can rapidly contaminate marine waters, preferentially moving through tidal channels (Paul et al. 2000). Increased retainment and use of on-site septic systems in Coral Gables cause contaminated groundwater release throughout

these high tide events, producing higher levels of wastewater tracers.

Effects of high amplitude tides on coastal waterway contamination are seen not only during king tide events but can potentially remain in Miami's waterways producing a vector for infection to bordering municipalities (Li et al. 2004, Rippy et al. 2013, Rodrigues et al. 2018). Local water residence time in Coral Gables and Wagner Creek appear to drive differences in fluoride and fecal coliform concentrations. This short-term king tide event analysis shows the importance of not only monthly sampling, but annual and event specific water sampling to monitor water quality. Extreme high tides pose threats to low lying communities as increasing sea level rise will lead to prominent concentrations of anthropogenic signatures and environmental stress on coastal urban waterways.

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