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Ecohydrology, Evapotranspiration and Hydrogeochemistry of Carbonate Mangrove Wetlands

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

ECOHYDROLOGY, EVAPOTRANSPIRATION AND HYDROGEOCHEMISTRY OF
CARBONATE MANGROVE WETLANDS

A dissertation submitted in partial fulfillment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY

in

GEOSCIENCES

by

David Lagomasino

2014

To: Dean Kenneth Furton
College of Arts and Sciences

This dissertation, written by David Lagomasino, and titled Ecohydrology, evapotranspiration and hydrogeochemistry of carbonate mangrove wetlands, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved

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Date of Defense: January 21, 2014

The dissertation of David Lagomasino is approved.

Dean Kenneth Furton
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University Graduate School

Florida International University, 2014

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DEDICATION

This dissertation is dedicated to my family. Their support, understanding, encouragement and love have made this dissertation possible.

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First and foremost, it has been an honor to have been mentored by a great advisor, Dr. René Price. Her commitment to the success of her students is unmatched, and because of her support and teachings I will leave here with the academic and research skills to succeed in academia, or wherever my future goals take me. I would also like to wholeheartedly thank my committee members, Drs. Dean Whitman, Assefa Melesse and Steven Oberbauer for their expertise, insights, knowledgeable critiques, and guidance during, and prior to, my doctoral candidacy. Besides the direction from my dissertation committee, Drs. Petya Campbell (NASA Goddard Space Flight Center) and Evelyn Gaiser have offered invaluable advice in support of my dissertation.

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ABSTRACT OF THE DISSERTATION
ECOHYDROLOGY, EVAPOTRANSPIRATION AND HYDROGEOCHEMISTRY OF
CARBONATE MANGROVE WETLANDS

by

David Lagomasino

Florida International University, 2014

Miami, Florida

Professor René M. Price, Major Professor

Coastal environments can be highly susceptible to environmental changes caused by anthropogenic pressures and natural events. Both anthropogenic and natural perturbations may directly affect the amount and the quality of water flowing through the ecosystem, both in the surface and subsurface and can subsequently, alter ecological communities and functions. The Florida Everglades and the Sian Ka'an Biosphere Reserve (Mexico) are two large ecosystems with an extensive coastal mangrove ecotone that represent a historically altered and pristine environment, respectively. Rising sea levels, climate change, increased water demand, and salt water intrusion are growing concerns in these regions and underlies the need for a better understanding of the present conditions. The goal of my research was to better understand various ecohydrological, environmental, and hydrogeochemical interactions and relationships in carbonate mangrove wetlands. A combination of aqueous geochemical analyses and visible and near-infrared reflectance data were employed to explore relationships between surface and subsurface water chemistry and spectral biophysical stress in mangroves. Optical satellite imagery and field collected meteorological data were used to estimate surface energy and evapotranspiration and measure variability associated with hurricanes and restoration efforts. Furthermore, major ionic and nutrient

concentrations, and stable isotopes of hydrogen and oxygen were used to distinguish water sources and infer coastal groundwater discharge by applying the data to a combined principal component analysis-end member mixing model. Spectral reflectance measured at the field and satellite scales were successfully used to estimate surface and subsurface water chemistry and model chloride concentrations along the southern Everglades. Satellite imagery indicated that mangrove sites that have less tidal flushing and hydrogeomorphic heterogeneity tend to have more variable evapotranspiration and soil heat flux in response to storms and restoration. Lastly, water chemistry and multivariate analyses indicated two distinct fresh groundwater sources that discharge to the phosphorus-limited estuaries and bays of the Sian Ka'an Biosphere Reserve; and that coastal groundwater discharge was an important source for phosphorus. The results of the study give us a better understanding of the ecohydrological and hydrogeological processes in carbonate mangrove environments that can be then be extrapolated to similar coastal ecosystems in the Caribbean.

TABLE OF CONTENTS

CHAPTER	PAGE
CHAPTER 1: INTRODUCTION	1
1.1 Objectives	2
1.2 Dissertation Organization	2
1.3 References	6
CHAPTER 2: ESTIMATING MAJOR ION AND NUTRIENT CONCENTRATIONS IN MANGROVE ESTUARIES IN EVERGLADES NATIONAL PARK USING LEAF AND SATELLITE REFLECTANCE	7
2.1 Abstract	7
2.2 Introduction	9
2.3 Study Sites	13
2.4 Methods	15
2.4.1 Site description	15
2.4.2 Water sampling and analysis	17
2.4.3 Spectral measurements	19
2.4.3.1 Leaf-level reflectance	19
2.4.3.2 Satellite-level reflectance	21
2.4.3.3 Spectral biophysical indices	23
2.4.4 Data Analysis	24
2.5 Results	27
2.5.1 Seasonal water chemistry	27
2.5.2 Mangrove spectral response: leaf-level	28
2.5.3 Mangrove spectral response: satellite-level	30
2.5.4 Relationship between vegetation spectra and water chemistry	31
2.6 Discussion	34
2.6.1 Water chemistry and mangrove spectral response	34
2.6.2 Regional-scale water quality	37
2.7 Conclusions	41
2.8 References	43
2.9 Tables	52
2.10 Figures	58
CHAPTER 3: SPATIAL AND TEMPORAL VARIABILITY IN SPECTRAL-BASED SURFACE ENERGY AND EVAPOTRANSPIRATION MEASURED FROM LANDSAT 5TM ACROSS TWO MANGROVE ECOTONES	72
3.1 Abstract	72
3.2 Introduction	74
3.3 Study area	75
3.4 Methods	77
3.4.1 Landsat 5 TM images	78
3.4.2 Satellite-based Energy budget and ET model	79
3.4.3 Meteorological Data	81
3.4.4 Data Analysis	82
3.5 Results	83
3.5.1 Spectral response	83

3.5.2 Energy Balance	85
3.5.3 Evapotranspiration.....	86
3.6 Discussion	87
3.6.1 Spatial and temporal variability.....	87
3.6.2 Storm damage response, recovery and long-term trends	94
3.7 Conclusions.....	98
3.8 References.....	101
3.9 Tables	107
3.10 Figures	111
CHAPTER 4: CONNECTING GROUNDWATER AND SURFACE WATER SOURCES IN A GROUNDWATER DEPENDENT COASTAL WETLAND: SIAN KA'AN BIOSPHERE RESERVE, QUINTANA ROO, MEXICO.....	123
4.1 Abstract.....	123
4.2 Introduction	125
4.3 Study Area	127
4.4 Methods	129
4.4.1 Peat Groundwater Wells.....	129
4.4.2 Water samples.....	130
4.4.3 Principal Component Analysis and End-Member Mixing Model	133
4.5 Results	134
4.5.1 Water chemistry.....	134
4.5.2 Water sources and principle component analysis	140
4.6 Discussion.....	144
4.6.1 End-member mixing	144
4.6.2 Nutrient dynamics.....	147
4.6.3 Groundwater/surface water disconnect in disturbed mangrove zone.....	149
4.6.4 Groundwater chemistry and groundwater discharge	150
4.7 Conclusions.....	154
4.8 References.....	156
4.9 Tables	162
4.10 Figures	179
CHAPTER 5: SUMMARY AND CONCLUSIONS.....	190
APPENDICES	194
VITA	204

LIST OF TABLES

TABLE	PAGE
Table 2.1. List of Landsat 5TM acquisitions and the respective day-of-year (DOY) that each image was captured.....	52
Table 2.2. Mean and standard deviations (SD) of the spectral indices calculated using Landsat 5TM at each site.....	53
Table 2.3. List of spectral indices, with their equations, that were determined using leaf reflectance and that have strong relationships with water chemistry.....	54
Table 2.4. Table of R values calculated from a regression analysis of leaf-scale based spectral indices and major cation and anion concentrations in the surface water (SW), shallow pore water (20cm), deep pore water (85cm), and groundwater (GW). Bold values indicate strong, significant ($p < 0.05$) relationships.	55
Table 2.5. Table of Pearson's correlation coefficients calculated from a regression analysis of Landsat 5TM band reflectance and derived spectral indices for mangrove sites in Shark River (SRS) and Taylor River (TS) with chloride concentrations in the surface water. Bold values indicate strong, significant ($p < 0.05$) relationships.	56
Table 2.6. Error analysis for satellite-derived surface water chloride model. PFE= Percent Forecast Error; MAPE= Mean Absolute Percent Error; RMSE=Root Mean Square Error; NRMSE= Normalized RMSE; CVRMSE=Coefficient of Variation RMSE. Y_t are the measured values, F_t are the modeled values, Y_{t+1} , is the next forecasted value, Y_{avg} is the mean of the measured values, Y_{max} and Y_{min} are the maximum and minimum of the measured values, respectively, and s_e is the standard error of the measured values.	57
Table 3.1. Average values and standard deviations of fractional vegetation cover (FVC), net radiation (R_n), soil heat flux (G), sensible heat flux (H), latent heat flux (λE) and evapotranspiration (ET) for each site. The units for R_n , G , H and λE are in $W\ m^{-2}$ and in $mm\ day^{-1}$ for ET.....	107
Table 3.2. Analysis of Variance p -values for fractional vegetation cover (FVC), net radiation (R_n), soil heat flux (G) and latent heat (λE) as affected by site location and decade with respect to each site. Bold values indicate greater than 95% confidence.....	108
Table 3.3. Error analyses table for measured versus modeled values energy balance parameters at TS6 and SRS6. PFE= Percent Forecast Error; MAPE= Mean Absolute Percent Error; RMSE=Root Mean	

	Square Error; NRMSE= Normalized RMSE; CVMSE=Coefficient of Variation RMSE. Y_t are the measured values, F_t are the modeled values, Y_{t+1} is the next forecasted value, Y_{avg} is the mean of the measured values, Y_{max} and Y_{min} are the maximum and minimum of the measured values, respectively, and s_e is the standard error of the measured values.....	109
Table 3.4.	Satellite-derived and field-measured net radiation (R_n), soil heat flux (G), sensible heat flux (H), latent heat flux (λE) and evapotranspiration (ET) at SRS6 for each Landsat 5TM image acquisition. The units for R_n , G , H and λE are in $W\ m^{-2}$ and in $mm\ day^{-1}$ for ET.	110
Table 4.1.	Summary of field parameters and stable isotopes for water sampling sites during the end of the wet season, from December 7-9, 2010.	162
Table 4.2.	Summary of field parameters and stable isotopes for water sampling sites during the end of the dry season, from May 5-9, 2012.....	164
Table 4.3.	Summary of alkalinity and major cations and anions for water sampling sites during the end of the wet season, from December 7-9, 2010.	167
Table 4.4.	Summary of alkalinity and major cations and anions for water sampling sites during the end of the dry season, from May 5-9, 2012.....	168
Table 4.5.	Summary of nutrient concentrations for water sampling sites during the end of the wet season, from December 7-9, 2010.....	171
Table 4.6.	Summary of nutrient concentrations for water sampling sites during the end of the dry season, from May 5-9, 2010.	172
Table 4.7.	Summary of saturation indices for major karst minerals and the log of pCO_2 for water samples collected from December 7-9, 2010.	174
Table 4.8.	Summary of saturation indices for major karst minerals and the log of pCO_2 for water samples collected from May 5-9, 2012.	175
Table 4.9.	Results of two principal component analysis (with alkalinity) shown as factor loadings for all principal components with the percent variability associated with each principal component.	177
Table 4.10.	Results of principal component analysis (without alkalinity) shown as factor loadings for all principal components with the percent variability associated with each principal component.	178

LIST OF FIGURES

FIGURE	PAGE
Figure 2.1.	Map of south Florida and the mangrove FCE LTER study sites in Shark River (✚SRS) and Taylor River (✚TS) located in Everglades National Park. Solid black symbols are the location of training set sites and the open symbols indicate the location of “test set” sites for the stepwise linear regression.58
Figure 2.2.	Box plots of water chemistry in the surface water (white), shallow pore water (light grey), deep pore water (medium grey), and groundwater (dark grey) from each site. The center horizontal indicates the median values and the upper and lower bounds of the box marks the first quartile (Q1) and third quartile (Q3). The whiskers represent the values that fall within $1.5*(Q1-Q3)$. Asterisks and open circles mark points between $1.5*(Q1-Q3)$ and $3*(Q1-Q3)$, and outside $3*(Q1-Q3)$, respectively.59
Figure 2.3.	Chloride concentrations in the groundwater and surface water at Taylor River (A) and Shark River (B), and in the shallow and deep pore water at Shark River (C) through time.60
Figure 2.4.	Annual total nutrient (TN) and total phosphorus (TP) concentrations, and TN:TP ratios in surface water (white) shallow pore water (light grey), deep pore water (medium grey), and groundwater (dark grey) from Shark River (SRS) and Taylor River (TS). The center horizontal indicates the median values and the upper and lower bounds of the box marks the first quartile (Q1) and third quartile (Q3). The whiskers represent the values that fall within $1.5*(Q1-Q3)$. Asterisks and open circles mark points between $1.5*(Q1-Q3)$ and $3*(Q1-Q3)$, and outside $3*(Q1-Q3)$, respectively.62
Figure 2.5.	Mean reflectance curves from red mangrove leaves at each station in Shark River (SRS) and Taylor River (TS) at different times of the year.63
Figure 2.6.	Seasonal mean leaf spectral reflectance curves of each mangrove species located at Shark River site, SRS6; red (dotted line), white (grey line) and black (black line).64
Figure 2.7.	Plot of <i>p</i> -values of ANOVA test comparing the differences in specific spectral wavelengths between sites (dark grey) and over time (black). A typical reflectance from a red mangrove is also plotted in light grey.65

Figure 2.8.	Mean Landsat 5TM reflectance values for each spectral band for sites at Shark River (SRS) and Taylor River (TS). Error bars coincide with ± 1 standard deviation.	66
Figure 2.9.	Graph of Landsat 5TM reflectance values for Landsat bands Band 2 (dark grey), Band 3 (light grey), and Band 4 (black), average surface water chloride concentrations (grey dots), and modeled chloride concentrations from stepwise regression (X) for Shark River site, SRS6 (left), and Taylor River site, TS6 (right).	67
Figure 2.10.	Scatter plots of selected relationships between reflectance indices (leaf-scale) and subsurface water chemistry. The equations and references for the listed indices are listed in Table 2.3.	68
Figure 2.11.	Plot of Landsat reflectance for Band4 and mean chloride concentrations at each site.	69
Figure 2.12.	Measured chloride concentrations versus modeled estimates (stepwise model) for the surface water. The grey dotted line represents a 1:1 relationship. The stepwise regression function was developed using the “training datasets” (SRS4, SRS5, SRS6, and TS6) and then “test datasets” (SH4 and TS8) were used to test the validity of the model.	70
Figure 2.13.	Map of modeled chloride concentrations along Shark River using Landsat 5TM reflectance data.	71
Figure 3.1.	Map showing the location of Florida (small inset), south Florida, Lake Okeechobee and Everglades National Park (large inset) and mangrove study sites in Everglades National Park.	111
Figure 3.2.	Scatter plot of net radiation (R_n) recorded at the tower at in Shark River and R_n recorded at the tower in Taylor River.	112
Figure 3.3.	Reflectance values of all visible and infrared Landsat bands and corrected surface temperature (Landsat Band 6) through time at dwarf mangrove site, (A) TS6 and tall mangroves, (B) SRS4 , (C) SRS-coast and (D) SRS6.	113
Figure 3.4.	Plots of Landsat 5TM-derived spectral indices, Normalized Difference Vegetation Index, Fractional Vegetation Cover and Soil-Adjusted Vegetation Index at (A) TS6, (B) SRS4, (C) SRS-coast, and (D) SRS6. The grey and black dashed lines indicated the arithmetic mean for SAVI and FVC, respectively.	114
Figure 3.5.	Multi-year average of net radiation (R_n), soil heat flux (G), sensible heat flux (H), latent heat of evaporation (λE) and Evapotranspiration (ET) for the 1990s and the 2000s for each site. Error bars denote 1 standard deviation.	115

Figure 3.6.	Measured versus modeled scatter plots of (A) net radiation (R_n), (B) soil heat flux (G), (C) sensible heat flux (H) and (D) latent heat (λE). Grey dashed line represents a 1 to 1 ratio.	116
Figure 3.7.	Satellite-based evapotranspiration (ET) rates in mm day^{-1} for each image acquisition at (A) TS6, (B) SRS-coast, (C) SRS4, and (D) SRS6.	117
Figure 3.8.	Multi-annual average of evapotranspiration for the 1990s and 2000s for each site. Error bars denote 1 standard deviation.	118
Figure 3.9.	Scatter plots of net radiation (R_n) versus latent heat (λE) and fractional vegetation cover (FVC) versus latent heat plots for each site.	119
Figure 3.10.	Map of modeled latent heat (λE) values in the tall mangroves in southwestern Florida near Shark River in (A) post-tropical storm conditions (March 1993 acquisition) and in (B) typical, “fair-weather” conditions (November 2008). Trajectories of tropical storms are shown in Figure 10A. Mangrove study sites are marked with black diamonds.	120
Figure 3.11.	Map of modeled latent heat (λE) values in the dwarf mangroves in southern Florida near Taylor River in (A) post-tropical storm conditions (March 1993 acquisition) and in (B) typical, “fair-weather” conditions (November 2008). Mangrove study sites are marked with black diamonds.	121
Figure 3.12.	Map of path, trajectory and strength of tropical storms and hurricanes that have made landfall near the study sites between 1990 and 2009. The strength of storm at initial landfall is shown. Storms that are underlined were of particular interest.	122
Figure 4.1.	(A) Map of the Sian Ka’an Biosphere Reserve showing the locations of study sites in the Bahia de la Ascension. False color composite Landsat 5 Thematic Mapper images for (B) Laguna Muyil, (C) Playon, (D) Rio Negro, (E) and Laguna Ocom.	179
Figure 4.2.	Picture, facing west, of Playon showing the undisturbed mangrove site (SKP-1) to the right (north) of the road, and the disturbed mangrove site (SKP-2) to the left (south) of the road.....	180
Figure 4.3.	Piper diagram showing major ion chemistry of water samples collected in the Bahia de la Ascension, Laguna Ocom, Playon, Rio Negro, and Laguna Muyil.	181
Figure 4.4.	Plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for water samples collected at each site in the Sian Ka’an Biosphere reserve. The global meteoric water line	

	(GMWL) is plotted as a grey line. The local evaporation line is plotted as a dotted black line.	182
Figure 4.5.	Bar charts of average (± 1 standard deviation) total nitrogen (TN), total phosphorus (TP) and TN:TP ratios plotted for samples from Bahia de la Ascension, Laguna Muyil, Laguna Muyil, brackish surface water from Playon and Rio Negro, pore water and groundwater.	183
Figure 4.6.	Semi-log plots of chloride concentration versus (A) total phosphorus concentrations, (B) total nitrogen, (C) total organic carbon, and (D) TN:TP ratios from all samples collected in the Sian Ka'an Biosphere Reserve. Outlying samples from sites SKRN-P (peten) and SKP-2 (disturbed mangroves) are circled in black.	184
Figure 4.7.	Log-log plots of (A) chloride (Cl^-) versus sulfate (SO_4^{2-}) concentrations and (B) $\text{Cl}^-/\text{SO}_4^{2-}$ versus $\text{Ca}^{2+}/\text{Na}^+$ sodium ratios for all water samples collected in the Sian Ka'an Biosphere Reserve.	185
Figure 4.8.	Water chemistry data from the Sian Ka'an Biosphere Reserve plotted in U-space as defined by the orthogonal projections from the principal component analysis. Recognized end-members are shown; Fresh groundwater, seawater, and peat groundwater. Outlying samples from SKP-2 (disturbed mangroves) are circled in black.	186
Figure 4.9.	Principal component plot (without alkalinity) for water chemistry data from the Sian Ka'an Biosphere Reserve plotted in U-space as defined by the orthogonal projections from the principal component analysis. Recognized end-members are shown; Fresh groundwater, seawater, and peat groundwater. Outlying samples from SKP-2 (disturbed mangroves) are circled in black.	187
Figure 4.10.	Stacked bar chart indicating the percentage of each end member, fresh groundwater (blue), seawater (orange), and peat groundwater (green) calculated for each water sample using the end-member mixing model.	188
Figure 4.11.	Plot of chloride versus calcium concentrations from water samples collected in the Sian Ka'an Biosphere Reserve. A conservative freshwater-seawater mixing line is plotted as a black line. Samples above the line indicate excess calcium.	189

CHAPTER 1: INTRODUCTION

The movement and quality of water is crucial for supporting environmentally sensitive and economically important ecosystems, such as tropical and subtropical coastal wetlands. These coastal environments are some of the most productive ecosystems that harbor many diverse biological habitats, and provide many economic benefits by way of hydrologic dampeners, filters and containments (Mitsch and Gosselink, 2000). In addition to the natural phenomena (e.g., tropical storms, sea-level rise, etc.) that can affect the stability of these coastal systems, growing hydrodynamic pressures from deforestation, eutrophication, water diversion, and other urban development practices have caused coastal wetlands to decline in recent decades (Valiela et al., 2001). In particular, mangrove ecosystems have seen a reduction of 30-50% over the past half century. Future climatic uncertainty, population expansion, and continued degradation to water flow and quality can jeopardize these valuable ecosystems.

Changes to the water quality, water movement, and timing of water flow play an important role in mangrove and estuarine productivity (Twilley and Rivera-Monroy, 2005). Biophysical stress in the form of nutrient limitations, eutrophication, and hypersalination can alter coastal vegetation community structure and function (Mitsch and Gosselink, 2000). Tropical and subtropical wetlands can have high evapotranspiration, which may exceed rainfall in particular months and years (Jiang et al., 2009) and because of this large atmospheric vapor supply, rainfall can be locally recycled or transferred to nearby regions (Price et al, 2008). Understanding the relationships linking the hydrology and ecology of coastal environments with natural and human-induced alterations are crucial to sustaining or mitigating coastal wetlands.

1.1 Objectives

The research sought to understand various ecohydrological, environmental, and hydrogeochemical interactions and relationships in carbonate mangrove wetlands. More specifically, the objectives addressed in this dissertation are:

1. to determine the spectral biophysical effects that surface and subsurface water chemistry have on the reflectance characteristics of mangroves;
2. provide a deeper understanding of the external mechanisms that alter evapotranspiration and surface energy in various mangrove environments; and
3. to investigate the groundwater and surface water interactions and hydrogeochemical flow paths in a karst mangrove wetland.

1.2 Dissertation Organization

The following three chapters in this dissertation were written to be submitted in peer-reviewed, scientific journals. Each chapter was written in accordance to the requirements of submission for the respective journals; and therefore, the references from each chapter are presented at the end of the chapter. The three main chapters were submitted to *Remote Sensing of Environment*, *Agricultural and Forest Meteorology*, and *Limnology and Oceanography*. Guidelines for authors from each of the journals are outlined in the appendices.

Chapter 2 (submitted to *Remote Sensing of Environment*) describes the relationship between water chemistry and electromagnetic reflectance in mangrove communities. A combination of surface and subsurface water chemistry, and electromagnetic spectral reflectance, data were analyzed from two physiologically distinct mangrove ecotones in Everglades National Park (ENP). The spectral reflectance characteristics of mangroves leaves measured using handheld spectroradiometers and passive satellites, and can change in response to a variety of different biophysical stressors, and more specifically from changes to the water chemistry and water quality that mangroves uptake for their biological functions. Seasonal and spatial variability in groundwater, pore water, and surface water chemistry resulted in similar seasonal dynamics in the spectral response of the mangroves leaves at both the field and satellite scales. Spectral data collected both in the field, and remotely via the Landsat 5 Thematic Mapper (TM) satellite sensor exhibited parallel responses to changes in water chemistry, such that when the ion concentrations were highest, the near-infrared reflectance was lowest. Similarly, mangroves in areas that were furthest inland experienced the greatest variability in both ionic concentrations and near-infrared spectral reflectance. Building upon these relationships between water chemistry and spectral reflectance, a stepwise linear regression model was used to closely approximate surface water chloride concentrations across the mangrove regions of the southern Everglades.

Decadal variability and disturbance impacts in evapotranspiration and surface energy are presented in Chapter 3 (submitted to *Agricultural and Forest Meteorology*). Sixteen Landsat 5TM images spanning 16 years from 1993-2009 were used to estimate energy budget and evapotranspiration in productively and hydrodynamically different mangrove

environments of the southern Everglades with respect to hurricanes and human modifications. A surface energy budget was used to model parameters such as net radiation, soil heat flux, sensible heat flux, and latent heat of vaporization using a combination of various satellite-based equations. Spectral variability recorded by satellite data was reflected in surface energy and evapotranspiration change. The greatest impacts and variability to the spectral properties, and in turn surface energy and evapotranspiration, of the mangroves occurred at sites with limited tidal flushing. At these limited-flushing sites, evapotranspiration rates were more closely linked with the fractional vegetation cover, while sites located along tidal channels displayed the most stable reflectance properties and evapotranspiration rates linked with net radiation.

Hydrogeochemical and multivariate analyses were conducted in a Yucatan carbonate mangrove estuary are presented in Chapter 4 (to be submitted to *Limnology and Oceanography*). These tests were used to explore the complex groundwater and surface water interactions in an environment that lacks major surface water bodies and relies heavily on groundwater movement. Water samples collected from the Sian Ka'an Biosphere Reserve described a complex hydrogeologic environment, heavily influenced by groundwater flow paths and coastal groundwater discharge. Using chemical and principal component analyses, two distinct fresh groundwater types were shown to discharge into the phosphorus-limited estuaries and shallow bays of the Reserve. The low levels of phosphorus along the coasts and in the bays of the Reserve suggest that brackish, coastal groundwater discharge may be extremely important for the delivery of limiting nutrients to the ecosystem.

The major findings, conclusions, and implications of this dissertation are summarized in Chapter 5. Future development of this research and the importance of understanding coastal wetland are also detailed in the last chapter. Following Chapter 5, the Appendices contains information related to the referencing style for each of the journals that Chapters 2, 3 and 4 were submitted to, as well chloride maps generated from remote sensing models, GPS coordinates for the study sites in Quintana Roo, Mexico, and schematics of groundwater wells installed in the Sian Ka'an Biosphere Reserve. Water chemistry data collected at SRS4, SRS5, SRS6, TS6 and TS7 in Everglades National Park will be readily available on the Florida International University Long Term Ecological Research (LTER) Program's data products website (<http://fcelter.fiu.edu/data/FCE>) once all the data are published in refereed journals.

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CHAPTER 2: ESTIMATING MAJOR ION AND NUTRIENT CONCENTRATIONS IN MANGROVE ESTUARIES IN EVERGLADES NATIONAL PARK USING LEAF AND SATELLITE REFLECTANCE

2.1 Abstract

Coastal mangrove ecosystems are under duress worldwide because of urban development, sea-level rise, and climate change, processes that are capable of changing the salinity and nutrient concentration of the water utilized by the mangroves. The present study correlates long-term water chemistry in mangroves, located in Everglades National Park, with spectral reflectance measurements made at both the leaf and satellite scale. Spectral reflectance measurements were collected using a handheld spectrometer for leaf-level measurements and Landsat 5TM data for regional coverage. Leaf-level reflectance data were collected from three mangrove species (i.e., red, black and white mangroves) across two regions; a tall mangrove (~18m) and dwarf mangrove (1-2m) region. The reflectance data were then used to calculate a wide variety of biophysical reflectance indices (e.g., NDVI, EVI, SAVI) to examine signs of stress. Discrete, quarterly water samples from the surface water, groundwater, and pore water (20 and 85 cm depths) and daily autonomous surface water samples were collected at each site and analyzed for major anions (Cl^- and SO_4^{2-}), cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}), total nitrogen (TN) and total phosphorus (TP). Mangrove sites that exhibited the highest salinity and ionic concentrations in the surface and subsurface water also had the lowest near-infrared reflectance at both the leaf and satellite-level. Seasonal reflectance responses were measured in the near-infrared (NIR) wavelengths at both the leaf and satellite scale and were strongly correlated with nutrient and ionic concentrations in the surface and subsurface water, even though there was no significant separability

between the three mangrove species. Study sites that experienced the greatest variability in surface and subsurface water ionic concentrations also exhibited the greatest fluctuations in NIR spectral reflectance. Landsat 5TM images were able to differentiate between tall and dwarf mangroves by the differences in spectral indices (e.g., NDVI, NDWI, and EVI) because of the variability in the background conditions amongst the environments. In addition, Landsat 5TM images spanning 16 years (1993-2009) were successfully used to estimate the seasonal variability in ionic concentrations in the surface water across the Florida Coastal mangrove ecotone. The study has shown that water chemistry can be estimated indirectly by measuring the change in spectral response at the leaf or satellite-scale. Furthermore, the results of this research can be extrapolated to similar coastal mangrove systems throughout the Caribbean and world-wide wherever red, black, and white mangroves occur.

2.2 Introduction

Mangroves are one of the most productive hydrologically controlled ecosystems that support high primary productivity, diverse habitats, and complex interactions between hydrogeology, biogeochemistry, and ecology (Twilley et al., 1992). These fragile ecosystems are sensitive to perturbations caused by human developments and both gradual (e.g., sea-level rise, saltwater intrusion) and abrupt (e.g., storms, temperature extremes) natural changes (Brunt, 1992; Mitsch and Gosselink, 2000). Coastal development has been a major cause of mangrove deforestation and coastal erosion, removing between 30-50% of the world's mangroves over the last half century (Valiela et al., 2001; Duke et al., 2007; Spalding et al., 2010). Populations along the coast are expected to increase over time and further intensify issues related to water quality and water availability (Vorosmarty et al., 2000; Lotze et al., 2006). In the Caribbean alone, 10% of the mangrove forests were lost in the 1980s as a result of deforestation, oils spills and other pollutants, and destruction of mangrove lands for urban and agricultural development (Ellison and Farnsworth, 1997). Since then, approximately one-third of mangroves have been lost globally between 1980s and 2000s (MA, 2005), continue to disappear more quickly than other endangered environments (e.g., coral reefs, tropical forests) and may disappear completely within the next century (Duke et al., 2007).

Changing the hydrology of these tropical and sub-tropical coastal wetlands can affect much of the surrounding ecosystem, from the food web dynamics (Winemiller and Jepsen, 1998; William and Trexler, 2006), community structure (Lugo and Snedaker, 1974; Twilley et al., 1992; Zedler and Kercher, 2005), and biogeochemical processes (Robertson and Alongi, 1992; Douglas et al., 2005). Moreover, coastal wetlands provide

many important ecosystem services. Some of the more economical services include flood mitigation, fish and seafood nurseries, recreation activities, water storage and filtration, and “blue carbon” sequestration (Ewel et al., 1998; Mitsch and Gosselink, 2000; Pendleton et al., 2012).

Hydrogeologic conditions and nutrient dynamics play an important role in mangrove productivity (Chen and Twilley, 1999; Twilley and Rivera-Monroy, 2005). Stable isotope studies have indicated that mangroves can become water stressed under phosphorus limited conditions (Lin and Sternberg 1992; Feller et al., 2003). Variable salinities and inundation times have also been shown to directly affect mangroves, leading to drought-like conditions (Clough, 1992). Soil and pore water phosphorus concentrations in the mangrove ecotone of the Everglades are higher along the southwestern coast (0.4-2.2 μM) than along the southeastern coast (0.4-0.8 μM) and are considered to be one of the causes of the tree height gradient from tall to dwarf mangroves, respectively (Simard et al., 2006; Mancera et al., 2009). These changing hydrogeologic and nutrient conditions can have an effect on the spectral reflectance properties of the plant leaves (Carter and Young, 1993; Govender et al., 2007).

Remote sensing and imaging spectroscopy have proved to be successful in measuring many environmental parameters. Some applications have included land cover classification, estimating biophysical factors and plant stress (e.g., leaf area index, light-use efficiency, water-use efficiency, and net ecosystem production), estimating energy balance components and evapotranspiration, and measuring water quality (Curran,

1989; Griffith et al., 2002; Williams and Norris, 2001; Hirano et al., 2003). The spectral range of 400 to 2700 nanometers (nm) covering the visible (VIS; 400-680) and near-infrared (NIR; 700-2700) wavelengths of the electromagnetic spectrum and is primarily used to study vegetation reflectance because most of the solar radiation occurs within these wavelengths. In addition, at wavelengths outside of this range (400-2700), atmospheric gasses (e.g., ozone and water) cause energy to be absorbed before it ever reaches the ground or canopy surface resulting in low and stable reflectance values of less than 5% (Knipling, 1970). Leaves typically exhibit a weak reflectance (i.e., strong absorption) in the VIS and NIR beyond 1300 nm. The absorption in the VIS is caused by chlorophylls, carotenoids and xanthophylls, which absorb in the blue (~450 nm) and red (~700 nm) wavelength and convert that energy to food through photosynthesis. The absorption characteristics beyond 1300 nm are primarily caused by the water content in the leaves (Allen and Richardson, 1968; Curran 1989). The high reflectance in the NIR is caused by the internal cellular structure (Mestre, 1935). The variations in reflectance of different wavelengths within the 400 to 2500 nm range can be used to calculate a number of predefined biophysical indices that have been related to leaf structure, biochemical content, and plant function (Roberts et al., 2011).

Imaging spectroscopy is useful for calculating spectra-derived biophysical indices that have been related to leaf structure, biochemical content, and plant function (Roberts et al., 2011). The biophysical indices are determined using specific wavelengths, or spectral derivatives in the visible (VIS) and near-infrared (NIR) portions of the electromagnetic spectrum that are sensitive to alterations in foliar chemistry (e.g., cellulose, lignin and chlorophyll) and plant membrane structure (e.g., chlorophyll and

water content), which have been shown to be altered by many environmental factors such as groundwater level, soil moisture, net radiation, water quality, salinity and nutrient limitations (Campbell et al., 2007; Naumann et al., 2008). Previous reflectance and biophysical studies have primarily focused on classification of vegetation or relating biophysical indices with other vegetation parameters (e.g., leaf area index, light use efficiency, biomass) and are primarily conducted in agricultural fields and temperate forests (Williams and Norris, 2001; Campbell et al., 2007) with some studies in mangrove wetlands (Ramsey and Jensen, 1996; Green et al., 1998; Hirano et al., 2003; Nichol et al., 2006; Kamaruzaman and Kasawani, 2007).

The reflectance properties of mangroves are dependent on the leaf structure and chemistry at the leaf-scale; and are dependent on the background and physical conditions such as exposed sediments (e.g., sand, peat), tidal cycles, soil moisture, leaf inclination, branches, and shadows at the canopy and satellite-scales (Hurcom et al., 1996; Diaz and Blackburn, 2003; Vaiphasa et al., 2005). Previous studies have addressed the role of water chemistry (e.g., salinity, major ions and nutrients) on leaf reflectance (Lauten and Rock, 1992; Ayala-Silva and Beyl, 2005; Poss and Russell, 2010). However, only a few have been applied in coastal areas (Naumann et al., 2008; Zinnert et al., 2011) and in tropical mangrove communities (Song et al., 2011). The present study seeks to understand the relationship between plant water source chemistry and mangrove leaf optical properties at both the site-specific and regional scales along an estuarine and productivity gradient. More specifically this study seeks to 1) characterize mangrove leaf spectral reflectance with varying surface and subsurface water chemistry, 2) identify spectral reflectance signatures between dwarf and tall

varieties of mangroves, and 3) identify the best approach to estimate surface and subsurface water chemistry from spectral reflectance data. To address these objectives, a combination of spectral data and water chemistry were collected together at two different mangrove communities along the southern coast of Florida, in Everglades National Park.

2.3 Study Sites

The Everglades sits on top of the Florida Carbonate Platform, which has an exceptionally low topographic gradient (slope of 3 cm km^{-1} ; Kushlan, 1989) and is composed primarily of highly permeable carbonate and siliciclastic sediments up to 2000-6000 m thick (Randazzo and Jones, 1997). The flat topography of the Everglades contributes to poorly defined watershed boundaries and a low hydraulic gradient (5×10^{-5}) (Price et al., 2006). Additionally, overland sheet flow is driven by the low topographical gradients and freshwater inputs from upstream, resulting in extensive surface flooding in both major waterways, Shark River Slough (SRS) and Taylor River Slough (TS) (Fig. 2.1). These two main waterways occupy underlying bedrock depressions $\sim 1.5 \text{ m}$ lower than the surrounding uplands (Gleason and Stone 1994; Obeysekera et al., 1999). The largest freshwater conduit, SRS (991 km^2) delivers water directly to the Gulf of Mexico but is only a fraction of its original pre-development size (Flora and Rosendahl, 1982). Taylor River Slough is located to the east of SRS and is separated by a relative topographic high (2-4 meters above sea level). Freshwater is delivered from TS to northern Florida Bay by way of a channelized creek system (Olmsted et al., 1980; Sutula et al., 2001) as a consequence of the presence of the Buttonwood Embankment, a 0.35

meter high near-continuous, natural coastal levee, which restricts overland flow and concentrates water into five major creeks (Orem et al., 1999; Sutula et al., 2001).

The Everglades is a hydrologically-controlled subtropical environment, where water levels, flows, and residence times play a crucial role in ecosystem function and structure (Light and Dineen, 1994). Annual precipitation in the region ranges between 1200-1500 mm yr⁻¹, and is unequally distributed throughout the year. Approximately 75-80% of the annual precipitation falls during the wet season between late May and November, with a bi-modal distribution of peak rains occurring in June and August (Duever et al., 1994; Windsberg 2003; Childers et al., 2006). The Florida Peninsula is prone to frequent afternoon thunderstorms and tropical cyclones during the late summer and early fall, and frontal systems with low temperatures and humidity in the later fall through early spring (Obeysekera et al., 1999).

Over the last 100+ years, anthropogenic compartmentalization of the northern Everglades via canals, levees and water conservation areas (Fig. 2.1) along with increased pressure of urban growth and development have resulted in an almost 50% reduction in the historical size of the Everglades (Walker and Solecki, 2004). Ultimately, these modifications to the Everglades region have not only reduced the natural flow of water into the ENP (approximately a 25% reduction in surface water flow into TS and >15% reduction into northeast SRS (Light and Dineen, 1994), but also altered the hydrogeologic and ecohydrologic dynamics of the mangrove ecotone (Rivera-Monroy et al., 2011). For instance, as water levels and flows decreased in ENP, seawater intrusion

into the coastal aquifer increased landward along the entire southern Florida coast (Fitterman and Deszcz-Pan, 1998; Price et al., 2006) allowing coastal mangroves to migrate over 1.5 km inland over the last 50 years (Simard et al., 2006; Rivera-Monroy et al., 2011).

2.4 Methods

2.4.1 Site description

The coastal mangrove forests of the Everglades consist of three mangrove species; *Avicennia germinans* (black mangroves), *Laguncularia racemosa* (white mangroves), and *Rhizophora mangle* (red mangrove) that also dominate many of the coasts of the Caribbean and South America. Mangroves were studied along two transects: one along SRS and the other along TS (Fig. 1). Some of the tallest (>18m) and most productive mangroves occur along the coastline of SRS (Chen and Twilley, 1999; Simard et al., 2006). Further inland of the coastline, the mangroves get progressively shorter and thinner, contain less biomass and are dominated by red mangroves and *Conocarpus erectus* (buttonwood) (Lugo and Snedaker, 1974; Chen and Twilley, 1999). Red mangroves comprise 35-90% of coastal mangrove forests with a biomass decreasing from ~250 to 90 Mg ha⁻¹ from SRS6 to SRS4 (Fig. 2.1), respectively (Chen and Twilley, 1999). The dwarf variation of *R. mangle* dominates (>99% abundance) the vegetation at each of the TS sites with sparse sawgrass and spike rush growing throughout the mangroves at the more landward site, TS6. Dwarf black and white mangroves also occur at TS7. The dwarf mangroves stand approximately 1-2 m tall and have a magnitude less in biomass accumulation relative to SRS mangroves, ranging between 9-23 Mg ha⁻¹.

Large homogenous stands of dwarf mangroves are disconnected in the coastal TS basin by a series of ponds and tidal channels.

All three SRS sites experience primarily diurnal tidal fluctuations (~1 m) with SRS4 having the least amount of fluctuation; however, during the wet season (June-October) more frequent tides exist because of higher water levels (Provost, 1973; Twilley and Chen 1998; Krauss et al., 2006). The tidal fluctuations along the TS coastline are small (~5cm) and primarily wind-driven because of the lack of circulation and connection with the Atlantic Ocean or Gulf of Mexico in the restricted, eastern portions of Florida Bay (Fig. 2.1) (Wang et al., 1994). The surface water salinity near the mouth of TS ranges between nearly fresh during the wet season and up to 30-50 PSU during the dry season (Brinceno et al., 2013). Surface water in TS flows towards the south to Florida Bay during the wet season, but may reverse directions during the dry season because of the relative topographic high along the coast, the Buttonwood Embankment, and lower water levels.

Five sites were monitored during this study and correspond to the research sites that are part of the Florida Coastal Everglades: Long-Term Ecological Research (FCE-LTER) program: SRS4, SRS5, SRS6 in SRS and TS6 and TS7 in TS (Fig. 2.1). Within each of the SRS sites, there were 3 stations (1, 2, & 3) that extended landward, perpendicular from the shoreline and were spaced 30-50 m apart. The SRS sites are located approximately 18.2 km (SRS4), 9.9 km (SRS5) and 4.1 km (SRS6) upstream from the river's mouth. Sites SRS4 and SRS6 have nearby groundwater wells (15.1 cm diameter) installed by the USGS that penetrate into the bedrock: SH2 (USGS ID 252436080574800; 3.75 m below surface) was located near SRS4; and SH3 (USGS ID

252150081044300; 7.33 m below surface) was located near SRS6. An eddy-covariance tower at SRS6 (~27 m above the surface), managed by Everglades National Park, measures environmental conditions such as; CO₂ flux, sensible heat, latent heat, solar irradiance, wind speed, air temperature and humidity at half-hourly intervals.

The Taylor River sites, TS6 and TS7 are approximately 1.6 and 4.4km from the coast, respectively. At the Taylor River sites, there were two shallow wells located at each site and a weather tower located at TS7 (Zapata-Rios and Price, 2012). The 3.81 cm diameter wells were installed just above the limestone bedrock, in the peat soils at both sites with an average depth of 0.5 m and 1 m below the surface at TS6 station and TS7, respectively. See Zapata-Rios and Price (2012) for more information about the well placement and construction.

2.4.2 Water sampling and analysis

Groundwater, surface water and pore water samples were collected every 2-3 months from February 2011 to December 2011; two sampling periods in the mid (February) and late (May/June) dry season and two samplings in the mid (August) and late (November) wet season. Groundwater samples (GW) in SRS were collected from two bedrock wells, SH2 and SH3 situated at sites SRS4 and SRS6, respectively. The SRS wells were purged using a dewatering pump and then sampled using a peristaltic pump. Two groundwater wells at each TS site were sampled by first purging three well volumes and then sampling using a peristaltic pump. Surface water samples were collected on the

same day as groundwater at each site in SRS (SRS4, SRS5 and SRS6) and at TS6 and TS7.

Pore water samples were collected at two depths; 0.20 m (PW-S) and 0.80 m (PW-D) below the surface, at the SRS sites. The pore water samples were collected using suction soil lysimeters, or “sediment sippers” (Montgomery et al., 1979; Fourqurean et al., 1992). A set of sippers were placed in the soils at each station along a transect perpendicular to the shoreline at each site. The air within each sipper was replaced with helium to remove any trapped oxygen. A vacuum pump was actuated to create a negative pressure of 15 inches of Hg in the sipper to draw water from the soil into the sippers. Water samples from the sippers were then collected within 48 hours of the initial deployment.

Water temperature, pH, specific conductance, and dissolved oxygen were measured in the field using an Orion multi-probe and a Thermo three-start pH meter at the time of sample collection. Unfiltered water samples were collected directly into acid-washed bottles and acidified with 10% HCl for total nutrient concentrations. Water samples collected for dissolved nutrients and ions were filtered through a 0.45 micron filter. Samples collected for cations were filtered and acidified with 10% HCl to a pH of less than 2. All samples were placed in a cooler on ice during transport to the laboratory and then stored in refrigerators at 4°C. Filtered water samples were analyzed for major anions (Cl^- and SO_4^{2-}) and cations (Na^+ , Mg^{2+} , K^+ , and Ca^{2+}) in the Hydrogeology Laboratory at FIU using a Dionex 120 Ion Chromatograph. Unfiltered water samples

were analyzed for total nitrogen (TN) and total phosphorus (TP) at FIU's Southeast Environmental Research Center (SERC) water quality laboratory. Total phosphorus (TP) was determined using a dry ashing, acid hydrolysis technique developed by Solarzano and Sharp (1980). Total nitrogen (TN) was measured using an ANTEK 7000N Nitrogen Analyzer using O₂ as a carrier gas instead of argon to promote complete recovery of the nitrogen in the water samples (Frankovich and Jones, 1998).

A continuous set of surface water samples were collected by an ISCO automatic water sampler (Teledyne) from January 2008 to January 2010. The ISCO sampler was located along the shoreline of the river channel at each of the sites. Each sample collected was a 1L composite sample containing four 250 mL subsamples collected every 18 hours. These extensive samples were collected once a month and brought back to the lab where they were then filtered and analyzed for major cations and anions as described above. Water samples collected from the ISCO sampler were binned into 3-day intervals and then averaged over the 3 year period from 2008-2011.

2.4.3 Spectral measurements

2.4.3.1 Leaf-level reflectance

The reflectance patterns of mangroves leaves from 120 individual trees across Taylor River and Shark River were measured in order to determine possible correlations with surface water, groundwater, and pore water chemistry. Three shore-perpendicular stations were located at each site in SRS and were selected on the basis of the distance from the main channel and the grouping of mangroves to include as many of the species

as possible near each station. The grouping of mangroves species was dependent on their location along SRS. The two sites in TS were almost entirely red mangrove stands and therefore, the white and black mangroves were not sampled at the TS locations. Leaf samples were collected from mangrove species that occurred at each station. Five replicates of each species were collected within a 5-10 m radius near each station and then analyzed for their leaf reflectance.

Leaves were collected four times throughout the year and coincide within the same week as the water samples. All leaf samples were quickly transported to the boat for reflectance analysis under direct sunlight conditions. High resolution leaf-level reflectance was measured using a Field Spec 3 and a Field Spec Handheld Spectroradiometer (Analytical Spectral Devices, Boulder, CO, USA). Spectral data were collected under the ambient light conditions of direct sunlight and cloudless skies. All spectral measurements were made using a 5° FOV at a distance of 1-2 cm from the leaf. Leaf radiance measurements were converted to percent reflectance by using a white Spectralon reference measured before and after each leaf sample. The adaxial surface of each leaf was measured and leaves from each tree were used to make an average spectral reflectance curve. Spectral reflectance was measured over the ranges of 325-1075nm (Field Spec Handheld) and 350-2500 nm (Field Spec 3) at a 1 nm spectral resolution. Leaf reflectance data were then used to calculate various biophysical indices that serve as indicators of biophysical stress conditions.

To help reduce the variability in spectral characteristics caused by differences in photosynthetic properties or water content at different heights in the canopy, leaves from the mangroves were collected in open, sunlit locations and from as high as possible in the tree canopy (~10 m above the ground surface). A total of ten healthy leaves (determined visually) were collected from each individual mangrove using extendable pole pruners. Leaves out of reach at the top of the canopy of the taller trees were not collected. However, samples were collected from trees in relatively open areas with the assumption that the leaves collected in lower levels of the tree canopy would receive similar levels of incident radiation from the sun as the top levels. Wang and Sousa (2009) showed that there was no significant difference in spectral characteristics between the leaves of mangroves in the upper and lower parts of the canopy. Differences in spectral characteristics were considered between dwarf (<2 m in height) and tall varieties of red mangroves. Dwarf red mangroves were sampled at the TS sites. Five leaves were sampled from the easily accessible crown of five individual trees at each station.

2.4.3.2 Satellite-level reflectance

Regional-scale variability across the Everglades was measured remotely using Landsat 5 Thematic Mapper (Landsat) imagery. Landsat includes 6 reflective channels in the VIS and NIR wavelengths with a spatial resolution of 30m x 30m and a thermal channel with a resolution of 60m x 60m. The three visible (VIS) bands include Band 1 (blue: 450-520nm), Band 2 (green: 520-600nm) and Band 3 (red: 630-690nm). The near-infrared (NIR) bands include Band 4 (760-900nm), Band 5 (1550-1750nm), and Band 7 (2080-2350nm). The thermal infrared band, Band 6, was not used in the study. Images from

Landsat were obtained from the US Geological Survey–Earth Explorer database and from the Florida International University Geographic Information Systems database.

Sixteen images that spanned 16 years from 1993 to 2009 were selected on the basis of minimal cloud cover over the Everglades (Table 2.1). Cloud cover was a major factor in selecting images in south Florida because of the nature of the wet season storm cloud development over the Everglades. Each satellite image (path:15, row:42) was atmospherically corrected and converted from radiance to reflectance using the ATCOR2 correction in ERDAS Imagine and subset, focusing primarily on the coastal mangrove ecotone. Spectral reflectance data were sampled and averaged from a 2 x 2 pixel subset of the corrected images covering 3600 m² (60m x 60m) at each of the sites, except TS7. Landsat imagery from TS7 was not used in the analysis because this site was near the southern margin of the scene and was not covered in many of the images. The pixels selected from each site were a minimum of 4 pixels (~120m) away from the main river channels to avoid spectral mixing with the open water or other vegetation as much as possible.

The 16 images used for this study were arranged with respect to the day-of-year (DOY) of image acquisition (Table 2.1). This arrangement corresponding to the DOY was done to obtain an average annual and seasonal variability that would not be possible within one actual year because of the lack of available cloud-free images. Arranging them according to the DOY provided a time series of images spanning the entirety of dry season, from November through May.

2.4.3.3 Spectral biophysical indices

A number of spectral indices were calculated using the leaf-level and satellite spectral data. Many of these spectral indices have been applied to a variety of different studies to measure leaf chemistry (e.g., chlorophyll, nitrogen, and lignin), water-use efficiency, and light-use efficiency (Roberts et al., 2011; Jones and Vaughn, 2011). These indices were used to establish correlations between the spectral characteristics and surface and subsurface water chemistry. A combination of reflectance and derivative ratios were applied to the hyperspectral leaf-level spectra collected from the mangrove leaves, as determined in other studies (Zarco-Tejada et al., 2003; Campbell et al., 2007). Many of the indices are band ratios of reflectance (R) or the derivatives (D) at narrow wavelengths between 400 and 1000nm (e.g., R760 or D780). To calculate the derivative of the reflectance spectra, the following formula was used:

$$D_{\lambda i} = \frac{R_{\lambda(i+1)} - R_{\lambda(i-1)}}{\lambda_{(i+1)} - \lambda_{(i-1)}} \quad (1)$$

where $D_{\lambda i}$ is the first derivative and $R_{\lambda i}$ is the mean reflectance of wavelength λ_i .

The coarser spectral resolution of the Landsat imagery prohibited the use of some of the hyperspectral indices and therefore leaf level spectra were compared to satellite spectra by applying widely used indices that were calculated for both spectral datasets. The Normalized-Difference Vegetation Index (NDVI) (Rouse et al., 1973), Normalized Difference Vegetation Index green (NDVIg) (Gitelson and Merzlyak, 1997), Normalized Difference Water Index (Gao, 1996) and the Enhanced Vegetation Index (EVI) (Huete et al., 2002) were derived using the following equations:

$$NDVI = \frac{Band4 - Band3}{Band4 + Band3} \quad (2)$$

$$NDVIg = \frac{Band4 - Band2}{Band4 + Band2} \quad (3)$$

$$NDWI = \frac{Band4 - Band5}{Band4 + Band5} \quad (4)$$

$$SAVI = \frac{Band4 - Band3}{Band4 + Band3 + L} * (1 - S) \quad (5)$$

$$EVI = G * \frac{Band4 - Band3}{Band4 + c_1 * Band3 - c_2 * Band1 + L} \quad (6)$$

where S , is a soil adjustment factor, c_1 and c_2 correspond coefficients of the aerosol resistance terms, L is the canopy background adjustment, and G represents a gain factor. The coefficients used in this study were adopted from Huete (1988) and Huete et al, (1994), where $S= 0.5$, $c_1=6$, $c_2=7.5$, $L=1$ and $G=2.5$.

2.4.4 Data Analysis

The ionic and nutrient concentrations analyzed from water samples and mangrove leaf reflectance collected from each station were compared to uncover possible relationships between water chemistry and physiological response linked to specific spectral bands and reflectance indices. Simple correlations were analyzed using a correlation matrix with water chemistry data (e.g., SW, PW-S, PW-S, and GW) and leaf-level spectra. The same methodology was applied to Landsat reflectance data and multi-year averages of major cation and anion concentrations in the surface water from each site. An Analysis of Variance (ANOVA) routine was applied to every hyperspectral band between 450 and 850nm (total of 400 spectral bands) to assess the variability in leaf-level spectral

reflectance between sites, as well as among dates of field measurements. Similar ANOVA tests were carried out on each of the Landsat multispectral bands and Landsat-derived spectral indices (e.g., EVI, NDVI, NDVI_g, NDWI, and SAVI) to assess the spectral differences across the mangrove communities and between the different sites and temporal variability of the satellite-based spectra. Comparisons between mangrove leaf spectra and water chemistry were also tested using ANOVA.

Reflectance values from each Landsat band were analyzed using a stepwise linear regression to determine correlations with water chemistry. Other studies have used stepwise linear regressions to fit observed chemical concentrations inside the leaf (e.g., nitrogen, chlorophyll) by using a combination of various spectral bands (Dawson and Curran, 1998; Kokaly and Clark, 1999; Curran et al., 2001). In my study, the stepwise linear analysis was used to develop a linear equation with coefficients, determined by the most important features (i.e., Landsat bands) to predict surface water chloride concentrations. The stepwise regression determines the most significant variables determined by a series of *F*-tests and *p*-values. For the present study, a backward stepwise regression was applied to the 6 optical Landsat bands. The Landsat bands were removed from the regression analysis when *p*-values for that particular band exceeded 0.5%, in order to determine the bands which contribute most to the variability in surface water chemistry.

A training data set was first used to develop the stepwise regression model. The training data set was composed of the three sites in Shark River and the dwarf mangrove site in

Taylor River. Once the model was generated, it was then applied to two test data sets to check for accuracy of the model. One test site was located in tall mangroves in Shark River (SH4) and one was located in the dwarf mangroves in Taylor River (TS8) (Fig. 2.1). These test sites were selected on the basis of the availability of long term salinity records and both sites were within the general hydrogeomorphic regions as the training set sites.

The accuracy of the chloride models was determined by a number of error statistics; root-mean-square-error (RMSE), normalized-root-mean-square (NRMSE), Nash-Sutcliffe, mean-absolute-percent error (MAPE), percent forecast error (PFE) and bias analyses. The RMSE was used to determine the deviation between the measured and model results but with the large range of chloride values spanning 2-3 orders of magnitude the NRMSE was used to normalize the RMSE to the range of values. The Nash-Sutcliffe index is widely used in hydrologic studies to calculate model efficiency but can be sensitive to sample size, outliers, and bias (McCuen et al., 2006). Therefore a bias analysis was also recorded with the Nash-Sutcliffe index. Lastly, MAPE and PFE analyses were also conducted where MAPE. The MAPE provided a percent error but could be skewed by higher percent errors when modeled values were larger than the actual values (Makridakis and Hibon, 1995). The PFE has been shown to be a good model for accuracy where with 95% confidence that the next time period will be within the PFE (Klimberg et al., 2010), Highly accurate models tend to have PFE values less than 20 (Lawrence et al., 2009).

Regional chloride concentration maps were generated for the Everglades mangroves using the stepwise regression model and the Landsat 5TM images. Non-mangrove areas (e.g., sawgrass, hardwoods, and water) were masked from each of the satellite images using the 1999 Vegetation Map of the Everglades generated by the University of Georgia (Welch et al, 1999) and available at the FCE LTER website (<http://fcelter.fiu.edu>). Once the mask was overlaid on each image, the stepwise model for chloride concentrations was applied to each of the mangrove pixels

2.5 Results

2.5.1 Seasonal water chemistry

Shark River and Taylor River both experienced fresh to brackish water conditions throughout the year and never reached typical seawater concentration. Study sites closest to the Gulf of Mexico (e.g., SRS6) and both Taylor River sites experienced the highest average ionic concentrations in the surface water, pore water and groundwater, while sites furthest inland, SRS4, tended to have the lowest average ionic concentrations (Fig. 2.2). The greatest variability in major cation and anion concentrations occurred in the surface water at each site, particularly at SRS4, TS6 and TS7 (Fig. 2.2). Pore water samples collected at 20 cm depth also tended to be highly variable throughout the year. Groundwater and deep pore water samples (85 cm depth) displayed the smallest range in ionic concentrations through the year, and exhibited a gradient of increasing concentration downstream. Peak ionic concentrations occurred during the May sampling, and the lowest concentrations occurred during the November sampling (Fig. 2.3A-2.3C). However, the groundwater at all sites tended to lag behind

the surface water and pore water and exhibited the highest concentrations in August after the overriding water became more fresh as a consequence of increased runoff from wet season rainfall (Fig. 2.3A & 2.3B). There was little difference in the water chemistry between the two Taylor River sites, except for slightly higher ionic concentrations in the groundwater at TS7. Surface water in Taylor River tended to be more fresh than the groundwater during the wet season (e.g., August and November sampling) and either similar or more brackish than the groundwater during the dry season (February and June sampling) (Fig. 2.3A).

The annual mean TP concentrations were lowest in the SW samples (TP=0.26-0.43 μM) and then followed by GW samples (TP=0.58-0.86 μM) at the sites in SRS (Fig. 2.4). Pore water TP concentrations across the SRS sites were an order of magnitude greater than the SW and GW, ranging from 1.51 to 8.71 μM . The highest TN concentrations in the pore water (PW-S and PW-D) were found at SRS4 (104-125 μM) and the lowest concentrations were found at SRS6 (67-100 μM) (Fig. 2.4). Pore water TN/TP values were lower than the surface water and groundwater across all sites and the lowest TN/TP values were found in the pore water at SRS6 (Fig. 2.4).

2.5.2 Mangrove spectral response: leaf-level

Mangrove spectra were measured for the three mangrove species found in the southern Everglades. However, because of the differences in mangrove communities between each of the sites, not all study sites were populated by all three species. All three species were measured at SRS6, but only red mangroves were measured at all study sites. Red mangrove leaf spectral reflectance was highly variable across the two

mangrove ecotones, exhibiting typical vegetation reflectance values with low reflectance in the VIS wavelengths (430-680 nm) and high reflectance in the NIR wavelengths (700-1100 nm) (Fig. 2.5). The range of reflectance values was also much lower in the VIS spectrum as compared to the NIR reflectance and only ranged between 1 and 15% in the blue and red wavelengths and 8-25% in the green wavelengths. The dwarf mangrove sites (e.g. TS6 and TS7) generally had the highest reflectance in the green wavelengths when compared to the tall mangrove sites; however, the variability in spectral reflectance between sites were significantly different ($p < 0.05$) at most wavelengths (Fig. 2.5).

Near-infrared reflectance was highly variable throughout the various sites ranging between 40 and 90% (Fig. 2.5). The greatest seasonal variability in NIR spectral response was measured at all stations at SRS4 and SRS5, and at station 1 at SRS6 (Fig. 2.5). The highest spectral return in the NIR reflectance (80-90%) at the aforementioned sites occurred during the wet season sampling in August and November, except for station 1 at SRS6 which occurred in June, during the late dry season (Fig. 2.5). Dwarf mangrove sites in Taylor River and stations 2 and 3 at SRS6 had the least amount of variability throughout the year in the NIR spectrum, and generally ranged from 50-80% reflectance. The results from the ANOVA tests for each of the spectral bands indicate that the spatial variability between mangroves sites was statistically significant ($p < 0.05$) for all of the spectral bands within the VIS wavelengths (Fig. 2.6). However, when compared to time of year, the differences between NIR spectra were found to be significant while no significant differences were found at the VIS wavelengths (Fig. 2.6).

All three species of mangroves were measured at SRS6 and at stations 2 and 3 at SRS5. The results from the ANOVA tests did not measure any significant difference ($p>0.05$) between the three mangroves species (Fig. 2.6). However, there was a significant relationship ($p<0.05$) between the NIR spectral response and the time of year similar to the relationship found with just the red mangroves (Fig. 2.7).

2.5.3 Mangrove spectral response: satellite-level

The reflectance values measured using the Landsat images and extracted from each of the mangrove sites exhibited some of the same characteristics identified at the leaf level. Similar to the leaf-level reflectance, the NIR bands of Landsat exhibited higher and more variable values than the VIS spectrum (Fig. 2.8). In addition, the range of values for Band 4 at TS6 was less than the ranges measured at the SRS sites. The SRS sites exhibited the highest average reflectance from Band 4 (30-36%), while the average Band 4 reflectance at the TS6 site was halved. Near-infrared reflectance from Band 5 and Band 7 was significantly higher ($p>0.01$) at TS6 than the reflectance at each of the SRS sites (Fig. 2.8). However, unlike the leaf level spectra, Band 3 reflectance values were significantly lower in the dwarf mangroves at TS6 when compared to the taller mangroves at SRS4, SRS5 and SRS6 (Fig. 2.8).

There was little temporal variability within Landsat Band 2 and Band 3 between each of the sites. In contrast, the NIR bands exhibited significant temporal variability across all sites. The mean Band 4 reflectance at TS6 was half the magnitude found in SRS (Figs. 8 & 9). A seasonal response was identified in the band reflectance at both mangrove

environments even though the indices did not show a significant difference (e.g. SRS and TS). There was a noticeable and significant decrease in Band 4 reflectance from November through May across each of the sites (Fig. 2.9). This time period from November to May corresponds to the dry season in south Florida (November-May). During the beginning of the dry season, Band 4 reflectance ranged between ~40-50% and decreased to 18-22% at the end of the dry season for the SRS sites and from 20% to 15-16% at TS6 (Fig. 2.9).

Various indices were calculated using the Landsat bands (e.g., NDVI, NDVIg, NDWI, SAVI, and EVI) and the means for each site are shown in Table 2.2. The results of an ANOVA test indicate that there was a significant difference ($p < 0.01$) in spectral indices between sites but not over time. The dwarf mangrove site, TS6, generally had a lower mean and higher variability for NDVI, NDVIg, and SAV with respect to tall mangrove sites (e.g., SRS4, SRS5, and SRS6). In contrast, EVI values, which include Band 1 in the computation, were significantly higher at TS6 and SRS4 than at SRS5 and SRS6 (Table 2.2).

2.5.4 Relationship between vegetation spectra and water chemistry

By combining the water chemistry data and the leaf and vegetation reflectance properties, we were able to identify relationships between nutrient and ionic concentrations, and mangrove leaf reflectance. Both the leaf and the satellite-level reflectance measurements exhibited similar responses to changes in water chemistry. At the leaf-level, various relationships emerged with a number of biophysical indices (Table 2.3 & 2.4; Fig 2.10). The spectral indices Rf_r , $D705/D722$, D_{max} and $RE3$ (equations

in Table 2.3) determined for red mangrove leaves were highly correlated with groundwater and pore water ion concentrations (Fig. 2.10A-2.10D). A positive relationship was noted between groundwater chloride⁻ and the spectral index RFf_r, and shallow pore water TP concentrations with D705/D722 (Fig. 2.10A & 2.10B). Negative relationships were exhibited between the derivative maximum (Dmax) around the red-edge inflection point (REIP) and shallow pore water Ca²⁺ concentrations, and between RE3 and SO₄²⁻ concentrations in the shallow pore water (Figs. 2.10C & 2.10D). Grouping the entire dataset of mangrove species together resulted in a negative and positive relationship between EVI, and deep pore water SO₄²⁻ concentrations and shallow pore water TN concentrations, respectively (Figs. 2.10E & 2.10F). The indices that best correlated with the water chemistry were ones that incorporated bands in the red and NIR wavelengths (Table 2.3 & 2.4).

Surface water chemistry exhibits a similar relationship with the Landsat reflectance as that seen with the leaf level data. There were strong, negative correlations between Band 4 reflectance and surface water chemistry, and more specifically chloride concentrations at each site (Table 2.5; Fig. 2.11). However, when all the sites were aggregated into the analysis, there was no simple correlation between Landsat bands or spectral indices and surface water chemistry (Table 2.5).

The stepwise linear regression that was applied to the Landsat data was used to help distinguish the Landsat bands that were most important in predicting surface water chloride concentrations across the mangrove ecotone. The backward stepwise

regression started with all 6 optical bands, and then removed bands that were not significant ($p>0.05$) to the overall model prediction using three steps. The most significant bands used to estimate surface water chemistry across all mangrove sites were Band 2, Band 3, and Band 4 to give the resulting equation ($R^2=0.51$; $p<0.001$):

$$[\text{Cl}^-] = A + (a_1 \times \text{Band 2}) - (a_2 \times \text{Band 3}) - (a_3 \times \text{Band 4}) \quad (6)$$

where A is a maximum chloride concentration (25100 mg L^{-1}) that can be detected, and a_1 , a_2 , and a_3 , are constants, 3220, 3270, and 712, respectively, expressed to three significant digits.

The Landsat spectral reflectance from each site was extracted from each image and then applied to the stepwise regression model defined in Equation 6 (Fig. 2.9 & 2.12). The accuracy of the satellite-derived surface water chloride model was tested with the addition of chloride and reflectance data from two nearby mangrove sites, SH4 and TS8 (Fig. 2.12). The modeled and measured chloride concentrations were highly correlated ($R=0.616$; $p<0.00$) and the results of a t -test ($df=64$; $t=0.511$) also indicate no significant difference between the two datasets (Fig. 2.12). The test data had a RMSE of 2948 and a NRMSE of 14.7 (Table 2.6). Even though there was a high RMSE, the magnitude of the of the chloride values spanned 2-3 order of magnitude ($\sim 400\text{-}20,000 \text{ mg L}^{-1}$) and is reflected in the small NRMSE. The Nash-Sutcliffe index was slightly low (0.36) and the MAPE was high (76) but occurred with a overestimate bias of -298 (Table 2.6). The PFE indicated that the model was highly accurate with a value of 9.81.

After the error analysis, Equation 6 was applied to each Landsat pixel in the mangrove environment to produce regional surface water chloride concentration maps showing

spatial and temporal variability across the Shark River area (Fig. 2.13). Modeled chloride concentrations in the Shark River showed a gradual increase in chloride concentrations moving through the dry season, with the lowest concentrations occurring in the November acquisitions and the highest during the May (Fig. 2.9 & 2.12). The temporal variability was also coupled with spatial variability which modeled a seaward gradient of increasing chloride concentrations (Fig. 2.12).

2.6 Discussion

2.6.1 Water chemistry and mangrove spectral response

The results of this study indicate that the seasonal variability in the chemical constituents of the groundwater, surface water and pore water can be estimated through the spectral response phenology of the mangrove vegetation from both the leaf-level and satellite level vegetation (Figs. 10 & 12). Other studies have suggested various biophysical relationships with plant spectra response such as LAI and NEP (Naumann et al., 2008; Campbell et al., 2013). Furthermore, studies have also suggested the link between subsurface water chemistry and spectral response with plant stress (Batelaan et al., 1998; Song et al., 2011). However, the present study has been unique with regard to understanding the relationship between surface and subsurface water chemistry in the mangrove zone at the site-specific and regional scale using the spectral reflectance of the mangroves.

At the site-specific scales, leaf spectral reflectance indices were strongly correlated with nutrient and ionic concentrations. Particularly, EVI did well estimating below ground

nutrient concentrations (Fig. 2.10). As nutrient concentrations (e.g., TN and TP) increased in the shallow pore water, EVI values also increased. The value of EVI has been used as a measure of “greenness” to effectively quantify various canopy structural variations and plant phenology and stress (Huete et al., 2002; Xu et al., 2011). High EVI values were associated with more nitrogen and lower sulphate concentrations and most likely represent periods of less biophysical and water stress. Therefore, as nutrients became available in the subsurface, the mangrove roots were selectively able to uptake the increased nutrients. Total phosphorus concentrations were highest in the pore water at SRS6 and also corresponded to the lowest TN/TP ratios, which suggests lower P-limitation at SRS6 (Fig. 2.4). The highest ionic concentrations were generally found at SRS6 and were typical at all sampling depths (i.e., SW, PW-S, PW-D, and GW). The variability observed in nutrient concentrations and TN/TP ratios has been identified in this region (Rudnick et al., 1999) and in conjunction with the higher ionic concentrations could help to explain the small variability and low leaf reflectance values of mangroves at SRS6. Studies have suggested (Kuenzler, 1969; Lugo and Snedaker, 1974) that mangroves in the presence of ample nutrient availability can still maintain high productivity regardless of low transpiration rates caused by increasing ionic concentrations in the water. Therefore, the leaf reflectance data supports this conclusion by suggesting that the mangroves at SRS6 exhibit signs of water stress (e.g., low NIR reflectance, low EVI), yet still have high biomass ($\sim 250 \text{ Mg ha}^{-1}$; Chen and Twilley, 1999) when compared to the upstream SRS sites with higher annual reflectance, more spectral variability, and lower biomass production.

The red, black and white mangroves in this region of south Florida were not able to be separated out by species based upon their reflectance spectra or through their reflectance indices (Fig. 2.7). Similar findings of indiscrimination between red, black, and white mangroves were also identified by Ramsey and Jenson (1996) in an area of the Everglades northwest of the SRS transect. However, mangroves in other parts of the world have been shown to have separability based on leaf spectral response under controlled conditions in the laboratory (Vaiphasa et al., 2005; Kamaruzaman and Kasawani; 2007). The relatively lower reflectances in the NIR of the mangroves at SRS6 relative to SRS4 and SRS5 have similar magnitudes and spectral variability as those measured by Ramsen and Jenson (1996) because many of their sites were located close to Gulf of Mexico and may have similar surface and subsurface water chemistry variability and hydrodynamics as SRS6.

There was little variability between the leaf spectral reflectance of the dwarf red mangroves at TS sites and the SRS6 site except for a slightly higher reflectance in the green wavelengths (~550nm), regardless of the significant biomass difference between the two areas (Fig. 2.5). The similarities between the mangroves at these 3 sites suggest that the stress factors enacted on the mangroves resulted in a similar spectral response, even though the biophysical stress factors (e.g., water chemistry, inundation frequency) may be different. The dwarf mangroves at the TS sites were considered to be in a stressed environment as noted from relatively heavier carbon isotope values in dwarf mangrove leaves versus tall mangroves leaves (-26.5 to -25.5‰ and -29 to -28‰, respectively; Lin and Sternberg, 1992; Feller et al., 2003). In addition, it has been shown that mangrove environments that are tidally flushed and exposed to higher nutrient

concentrations tend to be more favorable for mangrove productivity (Carter et al., 1973; Lugo and Snedaker, 1974). The intermediate biomass mangroves at SRS4 and SRS5 had elevated NIR reflectance during the wet season (e.g., August and November) and more variability throughout the year that were most likely caused by the greater annual fluctuations in ionic chemistry and greater phosphorus limitation indicated by the higher TN/TP ratios. During the wet season, pore water can be more readily flushed out, not only by greater precipitation but increasing surface water flows. The increasing amounts of fresh water and higher variability in water chemistry may cause various changes to the osmotic salt-tolerance regulating mechanism within the mangroves. Cells in the red mangrove leaves store high concentrations of sodium and chloride which make it an effective ion regulating filter (Parida and Jha, 2010) and most likely have an effect on the spectral response of the leaf as measured in this study (Fig. 2.2).

2.6.2 Regional-scale water quality

A relationship between Landsat 5TM reflectance and surface water chemistry was successfully obtained using a combination of band reflectance values and field measured water chemistry. Arranging the Landsat 5TM with respect to the DOY that the images were collected instead of the actual date of acquisition proved to be useful in understanding and modeling the surface water chemistry in the mangroves of the south and southwestern Everglades. In my study I only investigated the relationship between Landsat 5TM spectra and surface water quality because we were able to obtain a multiannual and semi-continuous datasets of surface water from each of the study sites.

The Landsat 5TM bands 1-3 (blue, green and red wavelengths) exhibited very little temporal and spatial variability between the SRS sites. However, there was a notable difference between the band reflectance at the SRS and TS sites. Reflectance from TM5 and TM7 measured at TS site was twice that of SRS sites while, Band4 reflectance at TS was half of the reflectance returned by the mangroves in SRS. This difference in VIS and NIR reflectance between TS and SRS was most likely a response caused by the different background conditions (e.g., soil, water, and vegetation) because of the variation in hydrogeomorphology between SRS and TS (Ramsey and Jenson, 1996; Diaz and Blackburn, 2003). The mangroves at SRS are tall and dense, producing thick canopies with a relatively higher LAI values (5.1-5.7; Cintron and Schaeffer-Novelli, 1983; Araujo et al., 1997). The SRS mangroves also tend to be aggregated onto larger islands that are disconnected by relatively wider river channels. In contrast, the dwarf mangroves found at TS are short and dense, have lower LAI values and are disconnected through a series of smaller tidal channels and pools (LAI=0.2-3.0; Cintron and Schaeffer-Novelli, 1983; Araujo et al., 1997). The heterogeneity of the background conditions in TS results in a mixture of reflectance signals (e.g., vegetation, water, and soil) recorded at the 30 m resolution of Landsat as compared to the relatively homogenous mangrove cover at the SRS sites. Despite the spectral mixing associated with the variety of background conditions at TS, there was still a significant correlation with the surface water chemistry at TS6.

The spectral indices calculated from Landsat data (e.g. NDVI, NDWI, SAVI, EVI) were able to identify differences between the mangroves sites. Averaged EVI, NDVI, and SAVI values were highest at SRS4 and generally the lowest at TS6 (Table 2.2). The EVI

number is related to canopy structure and plant physiology (Gao et al., 1996; Huete et al., 2002) which would suggest that the SRS4 has different biophysical traits than that from the other Shark River sites. The vegetation at SRS4 was a mix of red mangroves and buttonwood and was located near the transition zone between halophytes and glycophyte portion of Shark River (Lugo and Snedaker, 1974; Chen and Twilley, 1999). Therefore, the canopy structure is slightly different at SRS4 compared to SRS5 and SRS6. High EVI values and variability at TS6 are most likely related to the background conditions (Table 2.5). The NDVI and NDWI values are sensitive to chlorophyll (Gao et al., 1996) and liquid water content in leaves (Gao, 1996). Combining these indices together suggests that TS6 contains less chlorophyll and water in their leaves, but could also be related to background conditions.

There was a clear negative relationship between Band4 reflectance and surface water chemistry at each of the sites (Fig. 2.11). However, because of the variability in background conditions between the sites it was difficult to simplistically relate reflectance and water chemistry across all mangrove sites. A comprehensive model was developed to help address the temporal and spatial variability between mangrove types. The stepwise regression applied to Band2, Band3, and Band4 was able to reasonably estimate surface water chloride⁻ and the dry season variability for the two mangrove communities (Figs. 2.9 & 2.13).

The temporal and spatial variability modeled at the site-specific scale was also manifested at the regional scale (Fig. 2.12). Maximum chloride concentrations were modeled in the May Landsat 5TM acquisitions, and reached similar maximum values (20,000 mg L⁻¹) that have been observed in the region. The lowest concentrations were

modeled in the November satellite images. The low chloride concentrations in November are associated with the increase in freshwater flow during the wet season that continued to persist even though the heavy rainfall has subsided as a result of lag flow from upland sources. The combination of a decrease of freshwater runoff decreases, increases in evaporation and more influence from seawater contribute to the increase in Cl^- concentrations. The proximity to the coastline, as expected, also helps to establish a spatial pattern that is typical of most estuaries, where ionic concentration decrease upstream. This estuarine gradient was observed in Shark River where the model chloride concentrations were generally 2000-5000 mg L^{-1} higher along the coasts than in the interior portions of the mangrove ecotone (Fig. 2.12).

At higher measured chloride concentrations the model was an underestimate and at lower chloride concentrations the model was an overestimate (Fig. 2.12). The misestimate of chloride concentrations from the model could be caused by several climate related factors. Temperature extremes, humidity, water levels and storm effects that alter leaf dynamics and other physiological characteristics may have also had an impact on the variability of the canopy reflectance (Wang et al., 2008). The Landsat 5TM images cover a span of 16 years, and during that time and number of tropical storms (e.g., Hurricanes Andrew, Wilma, Katrina) and other periodic weather phenomena (e.g., El Niño Oscillations) have impacted the parts of the coastal mangrove environment. Additionally, ionic concentrations in the pore water and groundwater were not considered in the stepwise regression model which only utilized surface water chloride concentrations measured in the river channel adjacent to the mangrove sites. The present study has shown that variability in mangrove leaf reflectance may partially be caused by subsurface water chemistry and therefore, could contribute to the estimation errors of the stepwise function. However, even with the influence from climatic events

and lack of long-term pore water and groundwater information; there is still a significant relationship between average seasonal surface water chloride concentrations and mangrove reflectance.

2.7 Conclusions

My research examined surface and subsurface water chemistry and the spectral reflectance response of mangrove communities along an estuarine and productivity gradient in the southern and southwestern Everglades. Through a combination of field collected measurements and Landsat 5TM data, the findings of my research indicate a strong relationship between the chemistry of the possible plant water uptake sources in the coastal mangrove ecotone and the spectral reflectance response from the leaves of mangroves. Mangroves exhibited an indication of water stress in the NIR wavelengths (700-800 nm) when nutrients conditions were relatively low or when ionic concentrations were relatively higher. Similar connections have been described elsewhere with other coastal and mangrove communities; however, my research has built upon those previous studies and investigated relationships between multiple water sources and their chemical makeup, and the variability in productivity gradients in a coastal mangrove community. In addition, these relationships were applied to a generalized model that could estimate water quality on a regional scale.

Mangrove leaf and vegetation spectral reflectance exhibited seasonal and spatial signals of water stress and were successfully used to estimate ionic concentrations in the subsurface and surface water at the field and satellite-level. There were good

correlations between biophysical indices, particularly when the index incorporated NIR and VIS (red) wavelengths. The spectral reflectance and spectral indices from each mangrove, regardless of species, responded similarly to changes in ionic and nutrient concentrations. Dwarf mangroves and tall mangroves at SRS6 both exhibited similar reflectance responses at the leaf scale and suggest that both communities are water stressed by the higher ionic concentrations in the shallow groundwater and pore water, yet are drastically different in primary production. These relationships with water chemistry identified at the field scale were also measured in the satellite reflectance using the coarser resolution (30m x 30m grid) that aggregated the canopy cover as well as other background material (e.g., soils, water, and non-green plant material). Arranging the Landsat images in accordance with their DOY proved to be useful in robustly capturing the seasonal variability in hydrology along the coastal zones of both SRS and TS, despite the images not being collected from similar years and effects associated with tropical storms. The Landsat spectral signatures were different between the SRS and TS and are attributed to different background conditions based on the hydrogeomorphic variability between the two regions, but nonetheless are able to estimate the surface water chemistry in each region.

2.8 References

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2.9 Tables

Table 2.1. List of Landsat 5TM acquisitions and the respective day-of-year (DOY) that each image was captured.

Landsat 5TM Acquisition Date	DOY
November 17, 2008	321
November 20, 2003	323
January 3, 1997	3
January 20, 2003	20
January 25, 2005	25
January 31, 2007	31
February 5, 2009	36
February 18, 1996	49
February 26, 1999	57
March 11, 1998	70
March 29, 1993	88
April 1, 1994	91
April 23, 2008	114
May 4, 2006	124
May 6, 1995	126

Table 2.2. Mean and standard deviations (SD) of the spectral indices calculated using Landsat 5TM at each site.

Index	SRS4		SRS5		SRS6		TS6	
	mean	SD	mean	SD	mean	SD	mean	SD
EVI	2.76	0.53	1.47	0.78	1.26	0.63	2.56	6.42
NDVI	0.86	0.075	0.66	0.12	0.61	0.12	0.43	0.12
NDVlg	0.73	0.052	0.55	0.11	0.50	0.11	0.56	0.17
NDWI	34.51	5.24	36.58	7.80	30.70	7.84	16.51	3.26
SAVI	0.99	0.08	0.76	0.14	0.71	0.13	0.49	0.14

Table 2.3. List of spectral indices, with their equations, that were determined using leaf reflectance and that have strong relationships with water chemistry.

Index	Bands	Reference
C1	R_{695} / R_{760}	Carter, 1994
PRI1	$(R_{531}-R_{570}) / (R_{531}+R_{570})$	Gammon et al., 1992
PSRI	$(R_{680}-R_{500}) / R_{750}$	Merzlyak et al., 1999
Anthoc	$(1 / R_{550}) - (1 / R_{700})$	Gitelson et al., 2001
Dmax/D714	D_{max} / D_{714}	Entcheva-Campbell et al., 2004
D705/D722	D_{705} / D_{722}	Zarco-Tejada et al., 2002
EVI	$2.5 \cdot (R_{863}-R_{680}) / (R_{863}+6 \cdot R_{680}-7.5 \cdot R_{493}+1)$	Huete et al., 1994
RFf_r	$(R_{730}-R_{650}) / (R_{685}+R_{650})$	Campbell et al., 2007
RE3	Average R_{730} - R_{745}	Vogelman et al., 1997
Dmax	Derivative Maximum of red-edge	Sims & Gamon, 2002

Table 2.4. Table of R values calculated from a regression analysis of leaf-scale based spectral indices and major cation and anion concentrations in the surface water (SW), shallow pore water (20cm), deep pore water (85cm), and groundwater (GW). Bold values indicate strong, significant ($p < 0.05$) relationships.

Depth	Water chemistry	N	C1	PR11	PSRI	Anthoc	Dmax/ D714	D705/ D722	EVI
SW	Cl ⁻	82	-0.04	0.52	-0.44	-0.28	0.22	0.36	0.41
20 cm	Cl ⁻	55	-0.02	0.45	-0.24	-0.34	0.14	0.33	0.15
	SO ₄ ²⁻	55	0.03	0.38	-0.22	-0.23	0.00	0.34	0.12
	Na ⁺	55	-0.13	0.40	-0.12	-0.09	0.11	0.27	0.01
	K ⁺	55	-0.16	0.38	-0.12	-0.04	0.02	0.25	0.02
	Mg ²⁺	55	-0.12	0.39	-0.11	-0.08	0.09	0.26	0.01
	Ca ²⁺	55	-0.06	0.33	-0.19	-0.03	-0.02	0.34	0.11
	TN	45	0.27	-0.10	-0.57	-0.35	-0.34	0.32	0.63
	TP	45	0.20	0.21	-0.48	-0.55	0.28	0.58	0.43
	TN/TP	45	0.15	-0.37	0.36	0.57	-0.52	-0.32	-0.28
85 cm	Cl ⁻	72	-0.31	0.20	0.42	0.15	0.18	-0.24	-0.48
	SO ₄ ²⁻	72	-0.32	0.08	0.55	0.31	0.04	-0.30	-0.60
	Na ⁺	72	-0.26	0.22	0.40	0.13	0.21	-0.21	-0.46
	K ⁺	72	-0.22	0.17	0.39	0.17	0.10	-0.15	-0.45
	Mg ²⁺	72	-0.29	0.20	0.41	0.15	0.21	-0.21	-0.48
	Ca ²⁺	72	-0.23	-0.02	0.36	0.15	0.09	-0.18	-0.41
	TN	49	0.04	-0.20	-0.07	0.29	-0.50	-0.09	0.14
	TP	49	-0.17	0.24	-0.11	-0.20	0.22	0.16	-0.02
	TN/TP	49	0.15	-0.29	0.00	0.14	-0.29	-0.25	0.16
GW	Cl ⁻	65	-0.35	0.56	-0.01	-0.06	0.42	-0.08	-0.06

Table 2.5. Table of Pearson's correlation coefficients calculated from a regression analysis of Landsat 5TM band reflectance and derived spectral indices for mangrove sites in Shark River (SRS) and Taylor River (TS) with chloride concentrations in the surface water. Bold values indicate strong, significant ($p < 0.05$) relationships.

	Landsat 5TM Bands						Reflectance Indices				
	Band1	Band2	Band3	Band4	Band5	Band7	NDVI	NDVlg	NDWI	SAVI	EVI
SRS4	0.31	0.16	0.37	-0.53	0.54	0.47	-0.46	-0.44	0.63	-0.46	0.10
SRS5	0.58	-0.70	-0.45	-0.83	0.55	0.55	-0.20	0.14	0.72	-0.20	0.36
SRS6	0.25	-0.48	-0.07	-0.84	0.57	0.49	-0.65	-0.53	0.74	-0.65	0.28
SRS only	0.29	0.30	0.49	-0.53	0.19	0.26	-0.74	-0.69	0.42	-0.74	0.59
TS	0.17	-0.26	-0.43	-0.86	0.13	0.15	0.00	-0.12	0.11	0.07	0.20
SRS + TS	-0.12	0.38	0.28	-0.02	-0.18	-0.21	-0.19	-0.51	-0.20	-0.12	0.11

Table 2.6. Error analysis for satellite-derived surface water chloride model. PFE= Percent Forecast Error; MAPE= Mean Absolute Percent Error; RMSE=Root Mean Square Error; NRMSE= Normalized RMSE; CVRMSE=Coefficient of Variation RMSE. Y_t are the measured values, F_t are the modeled values, Y_{t+1} , is the next forecasted value, Y_{avg} is the mean of the measured values, Y_{max} and Y_{min} are the maximum and minimum of the measured values, respectively, n is the number of samples, and s_e is the standard error of the measured values.

Error Analysis	Equation	Values
PFE (%)	$(2 \times s_e / Y_{t+1}) \times 100$	9.81
MAPE (%)	$\Sigma(Y_t - F_t / Y_t) / n$	76
Nash-Sutcliffe	$\Sigma(Y_t - F_t)^2 / \Sigma(Y_t - Y_{avg})^2$	0.36
RMSE (mg L ⁻¹)	$\sqrt{\Sigma(Y_t - F_t)^2 / n}$	2950
NRMSE	$RMSE / (Y_{max} - Y_{min})$	14.7
Bias (mg L ⁻¹)	$\Sigma(Y_t - F_t) / n$	-298

2.10 Figures

Figure 2.1. Map of south Florida and the mangrove FCE LTER study sites in Shark River (+ SRS) and Taylor River (★TS) located in Everglades National Park. Solid black symbols are the location of training set sites and the open symbols indicate the location of “test set” sites for the stepwise linear regression.

Figure 2.2. Box plots of water chemistry in the surface water (white), shallow pore water (light grey), deep pore water (medium grey), and groundwater (dark grey) from each site. The center horizontal indicates the median values and the upper and lower bounds of the box marks the first quartile (Q1) and third quartile (Q3). The whiskers represent the values that fall within $1.5 \times (Q1 - Q3)$. Asterisks and open circles mark points between $1.5 \times (Q1 - Q3)$ and $3 \times (Q1 - Q3)$, and outside $3 \times (Q1 - Q3)$, respectively.

Figure 2.3. Chloride concentrations in the groundwater and surface water at Taylor River (A) and Shark River (B), and in the shallow and deep pore water at Shark River (C) through time.

Figure 2.4. Annual total nutrient (TN) and total phosphorus (TP) concentrations, and TN:TP ratios in surface water (white) shallow pore water (light grey), deep pore water (medium grey), and groundwater (dark grey) from Shark River (SRS) and Taylor River (TS). The center horizontal indicates the median values and the upper and lower bounds of the box marks the first quartile (Q1) and third quartile (Q3). The whiskers represent the values that fall within $1.5 \times (Q1 - Q3)$. Asterisks and open circles mark points between $1.5 \times (Q1 - Q3)$ and $3 \times (Q1 - Q3)$, and outside $3 \times (Q1 - Q3)$, respectively.

Figure 2.5. Mean reflectance curves from red mangrove leaves at each station in Shark River (SRS) and Taylor River (TS) at different times of the year.

Figure 2.6. Seasonal mean leaf spectral reflectance curves of each mangrove species located at Shark River site, SRS6; red (dotted line), white (grey line) and black (black line).

Figure 2.7. Plot of p -values of ANOVA test comparing the differences in specific spectral wavelengths between sites (dark grey) and over time (black). A typical reflectance from a red mangrove is also plotted in light grey.

Figure 2.8. Mean Landsat 5TM reflectance values for each spectral band for sites at Shark River (SRS) and Taylor River (TS). Error bars coincide with ± 1 standard deviation.

Figure 2.9. Graph of Landsat 5TM reflectance values for Landsat bands Band 2 (dark grey), Band 3 (light grey), and Band 4 (black), average surface water chloride concentrations (grey dots), and modeled chloride concentrations from stepwise regression (X) for Shark River site, SRS6 (left), and Taylor River site, TS6 (right).

Figure 2.10. Scatter plots of selected relationships between reflectance indices (leaf-scale) and subsurface water chemistry. The equations and references for the listed indices are listed in Table 2.3.

Figure 2.11. Plot of Landsat reflectance for Band4 and mean chloride concentrations at each site.

Figure 2.12. Measured chloride concentrations versus modeled estimates (stepwise model) for the surface water. The grey dotted line represents a 1:1 relationship. The stepwise regression function was developed using the “training datasets” (SRS4, SRS5, SRS6, and TS6) and then “test datasets” (SH4 and TS8) were used to test the validity of the model.

Figure 2.13. Map of modeled chloride concentrations along Shark River using Landsat 5TM reflectance data.

CHAPTER 3: SPATIAL AND TEMPORAL VARIABILITY IN SPECTRAL-BASED SURFACE ENERGY AND EVAPOTRANSPIRATION MEASURED FROM LANDSAT 5TM ACROSS TWO MANGROVE ECOTONES

3.1 Abstract

Coastal mangroves lose large amounts of water through evapotranspiration (ET) that can be equivalent to the amount of annual rainfall in certain years. Satellite remote sensing can play a crucial role in exploring the spatial and temporal variability of ET in isolated and inaccessible areas of coastal mangrove wetlands, like those found in Everglades National Park in southern Florida. Using a combination of long-term datasets acquired from the NASA Landsat 5TM satellite database and the Florida Coastal Everglades Long-Term Ecological Research project, the present study investigates how ET as well as radiation and other energy balance parameters in the Everglades mangrove ecotone have responded to multiple hurricane events and restoration projects over the past two decades. An energy balance model using satellite data was used to measure ET in tall and dwarf mangroves environments. An eddy-covariance tower and weather tower supplied long-term data of multiple environmental and meteorological parameters that were used in calibrating and testing the modeled results from the Landsat images. Results identified significant differences in soil heat flux measurements and ET between the tall and dwarf mangrove environments. The dwarf mangrove site had the highest soil heat flux and coincided with the lowest biophysical indices (i.e., FVC, NDVI and SAVI values) and ET rates. Mangrove damage and mortality associated with two strong hurricanes decreased FVC, NDVI, and SAVI, and increased soil heat flux at the tall mangroves site located in a basin-type environment. Recovery from the disturbance to the spectral characteristics, energy balance parameters and ET following

hurricanes was quicker in fringe mangroves than in basin mangroves. Evapotranspiration rates were also relatively high after each storm and may have increased as a result of elevated nutrient inputs from marine storm deposits. Remote sensing of the surface energy balance and ET of mangrove forests can help our understanding of how these environments respond to disturbances to the landscape and the effect that these changes can have on the energy and water budget. Moreover, relationships between energy and water balance components developed for the coastal mangroves of south Florida could be extrapolated to other mangroves system in the Caribbean measure these changes cause by natural events and human modifications.

3.2 Introduction

Evapotranspiration (ET) is a large component of the water cycle in subtropical and tropical wetlands (Rockstrom et al., 1999) and can amount to 70-110% of the annual rainfall in these regions (Sumner, 1996). The strong coupling between rainfall and ET in these regions can be attributed to high levels of rainfall recycling from high rates of ET (Eltahir and Bras, 1994; Price et al., 2008). Changes to ET induced by natural processes such as climate change and anthropogenic alterations such as land-use change can lead to regional variability and significant changes to the water budget (Pielke et al., 2002).

Remote sensing has been a proven tool to estimate ET rates and various other energy balance parameters across a variety of different ecosystems such as agricultural lands (Boegh et al., 2002), terrestrial forests (Chen et al., 2005), grasslands (Jiang and Islam, 2001) and wetlands (Chen et al., 2002; Jiang et al., 2009; Anderson et al., 2011). Measurements of ET over large areas are needed to support efforts aimed at modeling climate variability at global scales. Estimates of ET can be highly variable as a result of instrument calibration, model calculations and other environmental errors (Allen, 2000). However, a regional-scale evaluation of the spatial variability of ET across a coastal mangrove community will help to understand water budget variability associated with changes in mangrove productivity and in response to damage and recovery from tropical storms.

The present study seeks to understand the spatial and temporal variability of ET in the Florida coastal Everglades mangrove ecotone region (EMER) using a multi-year dataset of optical satellite images. More specifically, the study estimates the variability in ET and energy balance components between tall, riverine mangroves and dwarf, scrub mangroves. Additionally, this study investigates changes in ET associated with several storm events and the time needed for the mangroves to recover to pre-storm conditions.

3.3 Study area

The Florida Everglades once covered most of south Florida, extending from Lake Okeechobee south to Florida Bay and southwest to the Gulf of Mexico (Fig. 3.1). Most of the original Everglades has now been drained, channelized and converted to agricultural, urban and water conservation areas to support the growing population and the subsequent water demand (Light and Dineen, 1994; Chimney and Goforth, 2001). Water flow through the Everglades has been reduced by 15-25% of their original flows, allowing seawater to propagate upstream in the surface water and intrude landward in the aquifer (Fennema et al., 1994; Price et al., 2006). More than two-thirds of the 1.2 m annual rainfall in south Florida occurs during the wet season between late May and November, with peak rainfall occurring in June and August (Duever et al., 1994; Childers et al., 2006). During the wet season, the Florida peninsula is prone to daily thunderstorms and tropical cyclones, whereas in the dry season infrequent frontal systems account for much of the precipitation (Obeysekera et al., 1999).

An extensive coastal mangrove environment covers a large portion of the southern Everglades (~1445 km²) and has been migrating landward at a rate of 1.5 km in past 50 years (Simard et al., 2006; Rivera-Monroy et al., 2011). The landward transgression of mangroves has been attributed to reduced freshwater flow caused by the compartmentalization of the surface water upstream that is used to support the urban growth and development of south Florida. These anthropogenic, hydrologic modifications compounded with climatic factors (e.g., sea-level rise, storm events) ultimately alter the ecohydrologic and water cycle dynamics of the mangrove ecotone (Rivera-Monroy et al., 2011).

Two main conduits deliver water from the Everglades into Florida Bay and the Gulf of Mexico, Taylor River and Shark River (Fig. 3.1). Taylor River is the smaller of the two sloughs, and transports freshwater through a series of small, interconnected creek channels and discharges into the northeastern parts of Florida Bay (Olmsted et al., 1980; Sutula et al., 2001) (Fig. 3.1). Tidal fluctuations in Taylor River are primarily controlled by wind, as the eastern portion of Florida Bay is restricted from tidal exchange with the Gulf of Mexico and the Atlantic Ocean (Wang et al., 1994). During the dry season and the associated diminished freshwater flows, salinities in Taylor River can increase to 50 psu (Brinceno et al., 2013). Shark River is the largest slough (991 km²) and delivers water to the Gulf of Mexico after moving through relatively large and wide tidal channels along the southwestern Florida coast. Shark River experiences diurnal tidal fluctuations (~1 m) with progressively less tidal influence upstream of the Gulf of Mexico (Wdowinski et al., 2013). The largest tidal fluctuations occur during the wet

season when water levels are high because of increased freshwater flows (Provost, 1973; Twilley and Chen 1998; Krauss et al. 2006).

Mangrove forests line the coastal areas and tidal channels of both Taylor and Shark Rivers. Taylor River is predominately inhabited by the dwarf variety of *Rhizophora mangle* (red mangroves) that stand 1-2 m tall and has relatively low biomass accumulation rates (Coronado-Molina et al., 2004; Ewe et al., 2006). Along Shark River, the mangroves are a mix of three separate species; *Avicennia germinans* (black mangroves), *Laguncularia racemosa* (white mangroves), and *R. mangle* (red mangrove) that also dominate many of the coasts of the Caribbean and South America. Near the mouth of Shark River, all 3 mangrove species occur together and contain some of the largest and tallest mangroves in the region (Chen and Twilley, 1999; Simard et al., 2006). Upstream along Shark River, the mangroves become progressively smaller and shorter and the community structure changes to predominately red mangroves and *Conocarpus erectus* (buttonwood) (Lugo and Snedaker, 1974; Chen and Twilley, 1999). Red mangroves comprise 35-90% of coastal mangrove forests, and plant biomass decreases from ~250 Mg ha⁻¹ along the coast to 90 Mg ha⁻¹ at the inland extent of the EMER (Chen and Twilley, 1999).

3.4 Methods

Four sites were monitored and correspond to long-standing research sites that are part of the Florida Coastal Everglades: Long-Term Ecological Research (FCE LTER) program. Three mangrove sites were selected in Shark River; SRS4 (upstream), SRS6

(downstream), and SRS-coast (coastal) (Fig. 3.1). The upstream site, SRS4, is located 18.2 km from the mouth of Shark River, while SRS6 is located about 4.1 km from the mouth (Fig. 3.1). These two sites, SRS4 and SRS6, represent the freshwater and marine end-members, respectively, of the mangrove communities in the Shark River estuary. The third SRS site, SRS-coast, is located 1 km inland from the coast and located within a basin mangrove community, as characterized by Lugo and Snedaker (1974). One site, TS6, was monitored in Taylor River and represents the “typical” dwarf mangrove environment located in the Taylor River estuary (Fig. 3.1). An eddy-covariance tower at SRS6 measures environmental conditions such as CO₂ flux, sensible heat, latent heat, solar irradiance, wind speed, and air temperature. A second weather tower is located just south of TS6, but is restricted to half-hourly measurements of solar irradiance, wind speed and air temperature (Fig. 3.1).

3.4.1 Landsat 5 TM images

Landsat 5 Thematic Mapper data were obtained from the US Geological Survey-Earth Explorer database and from the Florida International University (FIU) Geographic Information Systems database. Landsat data consists of 7 bands in the visible [TM1 (blue: 450-520nm), TM2 (green: 520-600), TM3 (red: 630-690)], near-infrared (NIR) [TM4 (760-900nm), mid-infrared [TM5 (1550-1750nm), and TM7 (2080-2350nm)] and thermal infrared wavelengths [TM6 (10400-12500nm)]. The spatial resolution of each band is 30m x 30m, with the exception of the thermal band, TM6 which has a resolution of 60m x 60m.

Sixteen satellite images (path: 15; row: 42) were used in the study and covered a 16 year period from 1993-2009. The images were selected on the basis of minimal cloud cover and were confined to the dry season (November-May) because of a lack of cloud-free images during the wet season (June-October) when convective clouds form. Each of the satellite images were corrected for atmospheric effects using the ATCOR2 model in ERDAS Imagine. Atmospheric corrections were determined using solar geometry, a visibility of 35 km and solar and thermal regional models of rural and tropical conditions, respectively. After the satellite images were corrected, spectral reflectance data from each band was extracted from a 2 x 2 pixel block (3600 m²) from each of the Shark River sites, SRS4, SRS6, and SRS-coast and the Taylor River site, TS6. The extracted data from each site were averaged from each Landsat band and used to estimate the vegetation indices: normalized difference vegetation index (NDVI), soil-adjusted vegetation index (SAVI) and fractional vegetation cover (FVC), as well as energy balance parameters and ET.

3.4.2 Satellite-based Energy budget and ET model

Several energy balance parameters and ET rates were determined using Landsat images. Latent heat of vaporization (λE) estimates were calculated as the residual in the surface energy balance equation (Soegaard, 1989; Kustas et al., 1994; Boegh et al., 2002):

$$\lambda E = R_n - H - G \quad (\text{Eq.1})$$

where R_n is net radiation, H is sensible heat flux, and G is soil heat flux. The R_n component was estimated from the equation:

$$R_n = R_s (1-\alpha) + R_L (1-\varepsilon_s) - \varepsilon_s \sigma T_b^4 \quad (\text{Eq. 2})$$

where R_s is the incoming shortwave radiation, R_L is the incoming long wave radiation, α is the surface albedo, ε_s is surface emissivity (constant at $\varepsilon_s = 0.98$), σ is the Stefan Boltzman's constant ($\sigma = 5.6703 \times 10^{-8} \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-4}$) and T_b is surface temperature. Both R_s and R_L were measured directly from the eddy-covariance tower located at SRS6. Surface albedo, α , was estimated using a combination of Landsat bands, TM4 and TM7 as outlined in Brest (1987) and T_b was determined from the thermal band, TM6, of Landsat 5TM via the ATCOR2 model (Richter and Schlapfer, 2011).

The soil heat flux, G , was estimated by remote sensing techniques described by Clothier et al, (1986) and Kustas and Daughtry (1990). A soil-adjusted vegetation index (SAVI) was calculated using the following equation (Huete, 1988):

$$\text{SAVI} = (TM4 - TM3) / (TM4 + TM3 + 0.5) \quad (\text{Eq. 3})$$

The SAVI value was then used to determine the fractional vegetation cover, FVC (Ormsby et al., 1987; Purevdorj et al., 1998) using the linear equation:

$$FVC = 1.62 \times \text{SAVI} - 0.37 \quad (\text{Eq. 4})$$

A linear relationship between G and R_n has been noted for bare soils, but the (G/R_n) for vegetation can be different because of interactions with the canopy (Choudhury et al., 1987). Therefore, the FVC was used as a scaling factor in the equation

$$G/R_n = FVC (G/R_n)_{veg} + (1-FVC)(G/R_n)_{soil} \quad (\text{Eq. 5})$$

where $(G/R_n)_{veg}$ and $(G/R_n)_{soil}$ represent vegetation and soil end-member values and equal 0.1 and 0.5, respectively (Boegh et al., 2002). Daily ET rates (mm day^{-1}) were calculated using the equation:

$$ET = \lambda E / \lambda \quad (\text{Eq. 6})$$

where λ equals the latent heat of vaporization of water (2404 kJ kg⁻¹ for water with salinity of 20 at 20°C; Sharqawy et al., 2010). Sensible heat flux (H) was determined from the satellite-modeled R_n values using the equation:

$$H = R_n - G / (1 + 1/\beta) \quad (\text{Eq. 7})$$

where β is the ratio between H and λE , known as Bowen's ratio. A static value of $\beta = 0.603$ was used to calculate H at each site. The value of 0.603 was the 5-year average β (2006-2011) that was calculated from midday values of H and λE measured directly at SRS6. The numerator of Equation 7 was also treated as a constant where $R_n - G = R_n * 0.9$, with the assumption that G is approximately 10% of R_n .

The satellite energy balance model was designed using the model maker tool in ERDAS IMAGINE. Non-mangrove areas (e.g., sawgrass, hardwoods, and water) were masked from each of the satellite images using the 1999 Vegetation Map of the Everglades generated by the University of Georgia (Welch et al, 1999) and available at the FCE LTER website (<http://fcelter.fiu.edu>). Once the mask was overlaid on each image, Equations 1-7 were applied to each atmospherically corrected mangrove pixel which generated model estimates of FVC , R_n , H , G and λE across Shark and Taylor Rivers.

3.4.3 Meteorological Data

A suite of atmospheric and meteorological measurements were collected continuously from 2006-2011 from an eddy-covariance tower installed within the tall mangroves at SRS6. Explicit details of the instrument and tower deployment, specifications and corrections are outlined in Barr et al, (2010) and Barr et al, (2012). Measurements of

incoming solar radiation (i.e., R_s and R_l) at SRS6 tower were used in Equation 2 to calculate R_n at each of the Shark River study sites, SRS4, SRS6 and SRS-coast, and at the Taylor River site, TS6. Air temperature, G , H , and λE measured at the eddy-covariance tower at SRS6 were used to test and compare the results from the satellite-derived energy balance parameters. Meteorological data, such as net radiation and air temperature, were also collected at a weather tower south of TS6 (Fig. 3.1). Environmental data, tower and instrument specifications, and deployment methods for the Taylor River weather tower are described in (Zapata-Rios and Price, 2012). The R_n data recorded at SRS6 were slightly higher than the R_n recorded in Taylor River (Fig. 3.2). However, because of the similarity between the R_n values and the limited ground-truthing available in the Everglades, data measured at the Taylor River tower were used to validate the satellite-modeled results of R_n from Equation 2 at TS6. Average daily values for each year were derived by averaging midday (10:00-15:00h) measurements of each parameter for each day available of the 2006-2011 record. The daily data were then converted to a day-of-year (DOY) value to generate a 5-year daily average record. The latter dataset was then filtered through a 13-point moving average.

3.4.4 Data Analysis

An analysis of variance (ANOVA) was conducted to identify the temporal and spatial variability of the mangrove spectral response across the Everglades. Landsat reflectance values were organized according to site to identify relationships and differences between the various mangrove environments (i.e., fringe and basin) and mangrove types (i.e., tall and dwarf). Afterwards, 4 separate ANOVAs were then applied to the Landsat reflectance values that were grouped by decade, either 1990s or 2000s,

for each site to determine whether there were significant changes to the energy balance components over time.

The accuracy of the energy balance models was determined by a number of error statistics; root-mean-square-error (RMSE), normalized-root-mean-square (NRMSE), Nash-Sutcliffe, mean-absolute-percent error (MAPE), percent forecast error (PFE) and bias analyses. The RMSE was used to determine the deviation between the measured and model results but with the large range of chloride values spanning 2-3 orders of magnitude the NRMSE was used to normalize the RMSE to the range of values. The Nash-Sutcliffe index is widely used in hydrologic studies to calculate model efficiency but can be sensitive to sample size, outliers, and bias (McCuen et al., 2006). Therefore a bias analysis was also recorded with the Nash-Sutcliffe index. Lastly, MAPE and PFE analyses were also conducted where MAPE. The MAPE provided a percent error but could be skewed by higher percent errors when modeled values were larger than the actual values (Makridakis and Hibon, 1995). The PFE has been shown to be a good model for accuracy where with 95% confidence that the next time period will be within the PFE (Klimberg et al., 2010), Highly accurate models tend to have PFE values less than 20 (Lawrence et al., 2009).

3.5 Results

3.5.1 Spectral response

The greatest spectral variability in the Landsat reflectance data was exhibited in the near infrared band, TM4. At the Shark River sites, reflectance values in TM4 ranged from a low of 17% at SRS-coast to a high of 44% at SRS4 (Fig. 3.3). The TS6 site had less

variability and magnitude in TM4 and only ranged between 9% and 20% (Fig. 3.3). Reflectance data from the visible bands (TM1, TM2, and TM3) exhibited much less variability over the 16-year period of the Landsat acquisitions with the most variable reflectance at TS6. Mid-infrared bands, TM5 and TM7, tended to have a slightly stronger reflectance relative to the visible bands, except at the TS6 site. The reflectance in TM7 reached a maximum of 24-25% in May 1993 and May 2006 satellite acquisitions at SRS-coast; however, similar but smaller maxima occurred during the same periods at the other sites (Fig. 3.3). The thermal band, TM6, generally ranged between 10 and 33°C for each of the sites. Additionally, the highest temperature readings from TM6 tended to occur during acquisitions that had the lowest TM4 reflectance (Fig. 3.3).

At the riverine mangrove sites in Shark River, SRS4 and SRS6, there was little difference in spectral indices (i.e., FVC, NDVI, and SAVI), and they remained fairly consistent over the course of the 16-year Landsat dataset with little apparent change (Fig. 3.4). However, there were lower index values for each spectral index in March 1993 and May 2006 for all three Shark River sites and in particular, at the SRS-coast site (Fig. 3.4). The spectral ratios at the SRS-coast site were nearly 5 times lower than those from SRS4 and SRS6 March 1993 and slowly increased back to average values after 1996. In the May 2006 Landsat image, there was a relatively uniform drop in spectral index values across all three SRS sites (Fig. 3.4). The dwarf mangrove site at TS6 exhibited a different pattern from the mangroves in Shark River. Values across each of the spectral indices (e.g., NDVI, SAVI, and FVC) steadily increased over time from 1993 to 2009 (Fig. 3.4).

3.5.2 Energy Balance

The satellite-modeled R_n values were similar across most sites with decadal averages ranging between 487-524 W m^{-2} . The northern most site, SRS4, tended to have relatively lower R_n values (425 W m^{-2}) (Table 3.1). Sensible heat flux, H , measurements were similar to λE fluxes at SRS4 and SRS6. In contrast, λE was larger than H at SRS6 and lower than H at TS6 (Table 3.1). The Taylor River site, TS6 experienced the highest average G values (227 W m^{-2}) throughout the 16-year time period and the lowest average G was measured at SRS4 and SRS6 (129-140 W m^{-2} , respectively) (Table 3.1). Sensible heat fluxes closely mirrored the R_n for each site, accounting for slightly over 30% of the total R_n at each site. The FVC values that were used to calculate G were significantly lower at the TS6 site when compared to the tall, Shark River mangrove sites (Table 3.1).

During the 2000s, average G values were lower than fluxes from the 1990s at all mangrove sites, with the exception at SRS6 where the values remained constant (Fig. 3.5). The two largest drops in G were exhibited at TS6 and SRS-coast. The dwarf mangrove site, TS6, decreased from an average of 256 W m^{-2} in the 1990s to 199 W m^{-2} in the 2000s. The Shark River site, SRS-coast, also experienced a similar drop in G starting at 191 W m^{-2} in the 1990s and decreasing to 151 W m^{-2} and SRS4 dropped from 147 W m^{-2} to 111 W m^{-2} (Fig. 3.5). There was a decrease in average G values across three of the four mangrove sites, but only the reduction in G at SRS4 was significant ($p=0.05$) (Table 3.2). The other two sites, TS6 and SRS-coast, were still highly correlated but only 85% of the variability in G was associated with the change in decade (Table 3.2). Sensible heat fluxes remained relatively consistent over time.

Net radiation modeled for Shark River and Taylor River sites using Equation 2 and R_s and R_L data from the SRS6 tower provided R_n values that compared well with the actual field-measured R_n recorded at weather towers at SRS6 and TS6 (Fig. 3.6). Sensible heat flux, H , was calculated as a function of R_n (Eq. 7) and therefore, H values are correlated with modeled R_n . However, there was a greater deviation between measured and modeled H values (Fig. 3.6). Satellite-derived G measurements were overestimated and were nearly an order of magnitude higher for every Landsat acquisition date than the field-measured values at SRS6 (Fig. 3.6). The modeled average values for R_n , H and λE were in agreement with the field averages despite the variability between particular dates (Table 3.3; Fig. 3.6).

The accuracy of the satellite-derived energy balance model was tested with the addition using the measured parameters at the eddy-covariance tower at SRS6 (Fig. 2.12). The modeled data had a RMSE of ranging between 11.8 W m^{-2} for G and 53.0 W m^{-2} for R_n at SRS6 (Table 3.3). The Nash-Sutcliffe index was highest (0.71-0.88) for modeled R_n and λE values and lowest for G (-12.6), while the MAPE was lowest for R_n and λE and highest for G but occurred with an overestimate bias of -113 (Table 3.3). The PFE indicated that most of the models were highly accurate with PFE values below 20% for all the models except for G .

3.5.3 Evapotranspiration

Evapotranspiration rates modeled from Landsat images ranged between 3.5 and 13.7 mm day^{-1} at the Shark River sites and between 1.7 and 6.8 mm day^{-1} at the Taylor River

site (Fig. 3.6). The averaged ET rates were highest at SRS6 (7.9 mm day^{-1}) and lowest at TS6 (3.7 mm day^{-1}) (Table 3.1). Over the 16 year period of satellite acquisitions, ET rates remained relatively consistent through the 1990s and became more variable in the 2000s (Fig. 3.6). However, ET rates at SRS6 exhibited a different decadal variability with the highest rates occurring from 1992-1995 and then again in 2006 and 2008 (Fig. 3.7). Evapotranspiration modeled at the Taylor River site was always lower than ET at any of the Shark River sites (e.g., SRS4, SRS6, and SRS-coast). When the Landsat data were separated into decades (i.e., 1990s and 2000s) there was little change in the modeled ET rates between SRS4 and SRS6. However, there was an increase in average ET rates at SRS-coast and TS6; increasing from 5.9 to 7.5 mm day^{-1} at SRS-coast and from 3.1 to 4.4 mm day^{-1} at TS6 (Fig. 3.8).

3.6 Discussion

3.6.1 Spatial and temporal variability

Net radiation, G , H and λE varied between each of the mangrove sites. Satellite-derived ET rates at SRS4 remained relatively constant over the 16 year time period, even though the average R_n at SRS4 decreased from the 1990s to the 2000s (Table 3.3; Fig. 3.5). The decrease in average R_n in the 2000s could be explained by an increase in the mangrove coverage and biomass at SRS4 (Simard et al., 2006; Rivera-Monroy et al., 2011). Similarly, there was also a contemporaneous decrease in modeled G values at SRS4 over the same time period (Fig. 3.5). Modeled H values were relatively higher than λE values at TS6 and relatively lower than λE at SRS6. The magnitude of H values (100 - 250 W m^{-2} ; Fig 6) across all the study sites tend to be higher than typical H values found in subtropical and tropical forests (10 - 30 W m^{-2} ; da Rocha et al., 2004) and subtropical

wetlands ($20\text{--}70 \text{ W m}^{-2}$; Schedlbauer et al., 2011). The higher H values reported in the current study are an average of midday values, while the other studies reported daily values (da Rocha et al., 2005; Schedlbauer et al., 2011). The discrepancy between the modeled H fluxes in the present study could arise from the calculation used to determine H at each site. Bowen's ratio and the numerator in Equation 7 were kept constant throughout each of the Landsat images and could cause over or underestimates of H , depending on the time of year. However, there was still a fairly good agreement between measured and modeled H values (Table 3.3 & 3.4; Fig. 3.6).

The satellite-derived energy balance model estimates were in agreement with the measure values in Taylor and Shark River, except for G values (Table 3.3). Net radiation, H , and λE estimates each had MAPE of 10 or lower, and PFE values all under 20 suggesting the satellite model was a good predictor of the observed conditions. However, G values were always overestimated by an order of magnitude, which was one of the major limitations on the satellite-derived model. Nonetheless, despite the errors in G values the estimations of λE were still highly accurate. The over estimation of G in combination with accurate residual, λE , calculations suggests that energy was also dissipated by other factors, most likely from water and tidal actions.

The Bowen's ratio value of 0.603 used in the satellite-based surface energy balance equations implies that sensible heat should always be below the fluxes from λE . However, this was not the case at all the sites. Modeled H values were, on average, greater than λE at TS6 for the 1990s and the 2000s and during the 1990s for SRS-coast

(Fig. 3.4). Meanwhile, average λE was always higher than H at the two riverine mangrove sites, SRS4 and SRS6. Sensible heat flux values did drop from the 1990s to the 2000s and also occurred simultaneously with a decrease in G . The different relationships between H and λE at the riverine-type and basin-type mangroves suggest that there is less evapotranspiration in the basin-type mangroves. Yet ET modeled at SRS-coast resembles ET rates at SRS4 and SRS6. Bowen's ratio values around SRS6 can range between ~ 0.3 in the wet season and ~ 1.0 in the dry season (Barr et al., 2012). The eddy-covariance tower measures surface energy balance parameters without energy balance closure, whereas, with the satellite-based models, energy closure is needed to estimate λE .

Net radiation (R_n) was strongly correlated with ET rates at the Shark River sites SRS4 and SRS6, but had relatively less effect at the Taylor River site and SRS-coast site (Fig. 3.9A). The strong relationship between R_n and ET at the Shark River sites was most likely related to the spatial vegetation patterning between the Shark and Taylor River mangrove environments. The Shark River sites were predominately homogenous at the Landsat pixel scale (30 x 30 m grid) which was suggested by the small range of FVC values from each Landsat image where each pixel over the mangrove zone is either land or water (Fig. 3.9B). At the Taylor River site, the wider range of FVC values suggests that each Landsat pixel could be a combination of both vegetation and open water because of the smaller mangrove basal area ($2.3\text{--}6.3 \text{ m}^2 \text{ ha}^{-1}$; Coronado-Molina et al., 2004) relative to the larger basal area at SRS4 and SRS6 ($\sim 10 \text{ m}^2 \text{ ha}^{-1}$ and $40 \text{ m}^2 \text{ ha}^{-1}$ respectively; Chen and Twilley, 1999). Mixed pixels may also occur at SRS-coast directly after strong storm events which were suggested by the lower FVC values from

the mixing of background reflectance from soils or reflectance from damaged, defoliated mangroves (Fig. 3.9B).

The spatial differences between the Shark and Taylor River study areas were manifested in the *FVC*, *EVI*, and *NDVI* spectral indices calculated from Landsat images (Fig. 2.4). Satyanarayana et al, (2011) measured similar responses in *NDVI*, using multispectral data from the Quickbird satellite, from varying mangrove communities; larger, healthier sites generally had higher *NDVI* values and environmentally stressed sites typically had lower *NDVI* values. The highest variability in *FVC* was exhibited at SRS-coast and could be a function of storm related damage and the location of the mangroves in a basin-type environment (Table 3.1). In combination with the lower *FVC* values, TS6 also exhibited higher *G* values than the Shark River mangrove sites (Fig. 3.5). Soil heat flux has been shown to be sensitive to changes in vegetation cover because as vegetation covers and shades more ground, it dampens the incoming solar energy, and effectively attenuates the temperature transfer to the soil and thereby reduces *G* (Yang et al., 1999). Therefore, the higher soil heat fluxes measured at TS6 during the entire 16-year study period suggest that more energy was transferring to the soils and most likely, the water that inundates much of the Taylor River mangroves during the year.

Modeled λE values generally exhibited more spatial variability on the southwestern coast near Shark River than on the southern coast near Taylor River (Fig. 3.10). The southwest coast is primarily composed of a homogenous stands of mangroves over 8 m

tall with large basal areas, whereas the mangroves in around Taylor River are predominantly less than 4 meters and spatially discontinuous (Simard et al., 2006). The relatively homogenous modeled λE values in the dwarf mangroves around Taylor River was most likely related to the structure and low stature of the mangroves and the relatively stable shallow groundwater geochemical conditions as compared to the more variable (Zapata-Rios, 2009; Lagomasino et al., in review) (Fig. 3.11). In addition, Lagomasino et al, (in review) reported that the spectral signature of the dwarf mangrove leaves remain consistent throughout the year, and suggested that the stable shallow groundwater chemistry leads to more stable spectral reflectance values.

Evapotranspiration rates calculated for the current study derived from spectral data collected from Landsat with minimal inputs from field data (i.e., R_s and R_L) measured at SRS6. Satellite-based net radiation measurements agreed well with the field measured R_n values at SRS6. In addition, R_n values calculated at TS6 (using R_s and R_L inputs from the weather tower near TS6) also coincided with field-measured R_n (Fig. 3.6A). The consistently lower ET rates obtained at TS6 (Fig. 3.7) are associated with the higher G at TS6 in the energy balance equation, but moreover, could be related to a decrease in photosynthetic activity and transpiration in dwarf mangroves relative to tall mangroves (Hao et al., 2009; Naidoo, 2010). Hao et al, (2009) suggested the lowered photosynthetic activity in dwarf mangroves was caused by higher interstitial soil salinity and lack of tidal flushing.

Hydrogeomorphic and biophysical features along with restoration efforts between Shark River and Taylor River area may provide insight into the long-term changes to the energy balance parameters and ET in the Everglades mangrove region. The dwarf mangrove site, TS6, had an increase in averaged, satellite-based ET rates from the 1990s to the 2000s. The increase in ET at TS6 was in conjunction with an increase in *FVC* and a decrease in *G* (Fig. 3.4A & 3.7A). The cause of these trends over the recent decades may be linked to the growth and expansion of the dwarf mangrove patches in the Taylor River area in response to a variety of factors (Rivera-Monroy, personal communication, 2013).

The mangroves in the Taylor River area are separated from Florida Bay by the Buttonwood Embankment, a semi-continuous, 30-40 cm high band of storm deposit sediments that restricts tides and water discharge at certain times of the year (Wang et al., 1994; Michot et al., 2011). The Buttonwood embankment is a dynamic system that can change elevation and sediment composition, or can be reworked and redeposited during specific storm events (Davis et al., 2004; Lagomasino et al., 2013). Alterations to the embankment caused by storm events can create new discharge outlets, increase and redistribute nutrients, and deposit massive amounts of sediments. These processes could create conditions that are more suitable for the expansion of dwarf mangroves by adding allocthonous soil with higher nutrient concentrations in an area that is typically oligotrophic.

In addition to a number of storm events, several restoration projects have taken place in and around the Taylor Slough watershed that could have direct effects on the amount and quality of water that is delivered downstream to the mangrove ecotone. At the turn of the 21st century, two major restoration projects were underway to allow more water into the headwater region of Taylor River slough and to allow that additional water to pass through the watershed by expanding a bridge that had originally cut off flow from north to south. Sandoval et al, (in preparation) identified that flushing times in Taylor River, since the initial restoration project, were related to water discharge in the headwaters and suggested that an increase in surface water volume would decrease flushing times and lower ion concentrations in southern Taylor River. The change to the upstream surface water flow may help to flush out salinized soils in the dwarf mangrove region, increasing soil respiration and nutrient recycling in the process, and in turn reduce biophysical stress among the mangroves.

The mangroves along Shark River are generally inundated once to twice a day depending on the time of year and the tides (~1 m) (Provost, 1973; Twilley and Chen 1998; Krauss et al. 2006) and therefore, the mangrove sediments tend to be flushed regularly and with greater marine influence. Moreover, burrowing crabs at sites similar to those in Shark River have been shown to increase the hydraulic conductivity of low-permeability mangrove sediments (Gleeson et al., 2013). The increase in flushing at Shark River mangrove sites provides better growing conditions allowing the mangroves to utilize more water and nutrients to produce higher biomass relative to the Taylor River mangroves and therefore, have high spectral index values (e.g. NDVI, SAVI and EVI), and ultimately, higher ET.

3.6.2 Storm damage response, recovery and long-term trends

South Florida is prone to tropical cyclone activity and has had a number of tropical storms and hurricanes pass over or near the study area over the 16 year time span of the Landsat data (Fig. 3.12). Three hurricanes during that time period of are particular interest because they were significant storms and coincide closely with Landsat image acquisitions: hurricanes Andrew (1992), Katrina (2005) and Wilma (2005) (Fig. 3.12). Weaker tropical storms including Harvey (1999), Irene (1999), Ernesto (2006) and Fay (2008) also passed effected the study area (Fig 12).

Mangroves are well adapted and resilient against storm conditions. However, after strong storms, larger mangroves with a diameter-breast-height (DBH) greater than 5 cm have a significantly higher chance of mortality than smaller mangroves (Smith et al., 1994; Risi et al., 1995). Additionally, Smith et al, (1994) documented a nearly 50% increase in mangrove mortality rates months and years after the passing of hurricane Andrew (category 4) through south Florida in August 1992. The observation of initial tree mortality directly after the storm followed by a continued increase in post-storm mangrove mortality, associated with storm surge damage and salinization, may be the cause of the higher mid-NIR response (Fig. 3.2) and lower vegetation index response (Fig. 3.4) noted in this study at SRS-coast. Fractional vegetation cover, NDVI, and SAVI values were at their lowest at SRS-coast in the 3 years following hurricane Andrew. Likewise, the spectral indices were also lowest at the TS6 directly after hurricane Andrew. Low FVC, NDVI and SAVI values also occur across all three Shark River sites in the May 2006 Landsat image, which occurred a few months after the passage of hurricanes Katrina and Wilma in 2005.

Previous studies have indicated that the structure of mangroves stands can influence the disturbance effects caused by storms (Ward et al., 2006). Surveys conducted after hurricane Andrew and hurricane Wilma identified higher mangrove mortality rates in basin-type mangroves after hurricane Wilma, but relatively more damage was caused to island and fringe-type mangroves after the passage of hurricane Andrew (Smith et al., 2009). The local minimums in *FVC*, *NDVI*, and *SAVI* measured from the Landsat images March 1993 and May 2006 suggest significant damage to the mangroves at each of the Shark River sites following hurricanes Andrew and Wilma with the greatest detriment occurring at SRS-coast which were indicated by the much lower index values (Fig. 3.4C). Barr et al (2012) presented a similar spectral index (i.e., *EVI*) response after hurricane Wilma using MODIS. The relatively quick recovery (~1 year) suggested by the Landsat data is also mirrored in the MODIS *EVI* data where *EVI* values return to pre-Wilma conditions approximately one year after the storm (Barr et al., 2012). The drop in spectral vegetation indices, *FVC*, *NDVI* and *SAVI*, recorded in acquisitions following hurricanes Andrew (1992) and Wilma (2005) was most likely caused by a combination of defoliation and tree mortality from strong winds during the hurricane and the subsequent storm surge.

Despite the surveys conducted after hurricane Andrew identifying most of the damage areas in fringe and island mangroves (Smith et al., 2009), there was very little change in spectral values at SRS4 and SRS6, both fringe mangrove sites, as opposed to the damage done in the basin mangroves at SRS-coast. The eye wall of hurricane Andrew passed just north of the SRS4 and SRS6. However, storm surge (1-4 m) related to the southern eyewall flooded the mangrove wetlands up to 10 km inland and deposited up to

20-50 cm of carbonate-rich muds (Risi et al., 1995; Swiadek, 1997). The resulting surge and reduced tidal flushing in the basin mangroves around SRS-coast can be the cause of the increased mangrove mortality at SRS-coast relative to SRS4 and SRS6, and the reason there was a more significant drop in FVC and other spectral indices at SRS-coast.

In addition to the spectral response, the modeled G values from SRS-coast and TS6 exhibited a decrease from the 1990s to the 2000s (Fig. 3.5). Occurring in tandem with the lower average G values in the 2000s, average λE and ET increase over the same time period. The decrease in G at SRS-coast and TS6 can be attributed to an increase in vegetation growth and mangrove recovery following hurricane Andrew. Reflectance values in TM1 and TM3 also decrease from 1993 to 2009 at the TS6 site suggesting increased absorption from photosynthetic pigments caused by new leaf growth in the dwarf mangroves at Taylor River (Fig. 3A). Recently, researchers have measured an increase in above ground net primary production of mangroves from $\sim 1800 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 2001 to $\sim 5800 \text{ g C m}^{-2} \text{ yr}^{-1}$ in 2004 at a site near TS6 (Ewe et al., 2006) as well as an increase in dwarf red mangrove patch size from 2003 to recent (Rivera-Monroy, personal communication, 2013). The combination of a steady increase in FVC and steady decrease in G at TS6 can be directly linked to increased dwarf mangrove production as individual mangrove patches have grown larger. River discharge has not shown any significant increase since the inception of the Taylor River Slough restoration despite recent studies indicating a strong link between water flushing times and freshwater input (e.g., local management practices) (Sandoval et al., in preparation). Therefore, the increase in ET and FVC at TS6 may be related to short-term changes in sea-level that have been more conducive to the growth and expansion of mangroves (e.g., nutrient inputs).

Sharp increases in satellite-based ET rates were identified after storm events (1993 & 2005) at the SRS6 site (Fig. 3.7). Evapotranspiration rates measured at SRS4, SRS-coast, and SRS6 sites were relatively equal throughout the study period, except for time periods directly after strong storm events when satellite-based ET rates at SRS6 were nearly double the rates at SRS4 and SRS-coast. A possible explanation for the higher ET rates at SRS6 directly following hurricanes could be from increased nutrients that were brought onshore by the storm surge associated with the passage of hurricanes Andrew and Wilma. Phosphorus-limited mangrove environments, like in the Shark River and Taylor River portions of the Everglades, have been shown to have low leaf water potential, low stomatal conductance, photosynthetic carbon-assimilation rates, and less conductive xylem (Lovelock et al., 2006). However, Lovelock et al, (2006) noted that these water-stress related factors were mitigated when more P was added to the system. The storms deposits from hurricane Wilma showed a relative increase in Ca-bound P (20-25% of total P pool) compared to the composition from the top soil (Castañeda-Moya et al., 2010). Higher ET rates at SRS6 could also be related to the increase in R_n as it reaches a maximum in May. Nevertheless, elevated ET rates were only observed at SRS-6 and therefore suggest the increase in ET after storms was associated with biological productivity rather than atmospheric.

The regional maps of λE that were generated using Landsat imagery demonstrate the variability in the mangroves and their response to strong tropical storms and in steady state conditions for the Shark River area (Fig. 3.10) and Taylor River area (Fig. 3.11). The southwestern mangroves in the Shark River vicinity exhibited high spatial variability in λE values images collected within 1-3 years after the storm (Fig. 3.10A). Latent heat

values were highest in the islands around SRS6 and along Shark River, whereas to the north, λE values were much lower. Many of the mangroves north of Shark River are separated from tidal channels and were also along the trajectory of the tropical storms (Fig. 3.10A). However, the λE map identifies two responses the mangroves have after storms; 1) mortality and defoliation from storm surge and high winds (Smith et al., 1994), and 2) and elevated λE values in areas with large phosphorus-rich sediment deposits and regular tidal flushing. Under more meteorologically stable conditions, for instance the November 2008 map, indicates more homogeneity in λE values across the mangroves most likely related to forest regrowth and recovery (Fig. 3.10B).

The λE values for mangroves along the southern coast around Taylor River remained generally consistent throughout the region and for the most part were independent of the storm conditions (Fig. 3.11). In the March 1993 image collected after hurricane Andrew, the modeled λE values were low ($180\text{-}260\text{ W m}^{-2}$) across the dwarf mangrove region (Fig. 3.11A). Fifteen years later in November 2008 the λE values in the dwarf mangroves have increased, yet still have little spatial variability ($300\text{-}360\text{ W m}^{-2}$) and most likely reflect the increase in mangrove basal area (Rivera-Monroy, personal communication) (Fig. 3.11B).

3.7 Conclusions

The Everglades have endured numerous modifications from both human engineering (e.g., canals, levees) and natural events (e.g., tropical storms, sea-level rise). Long-term datasets acquired from the NASA Landsat mission and the FCE LTER project have

provided insight into the spatial and temporal variability of ET and energy balance components in the Everglades, and more specifically, how the mangrove ecotone has responded to multiple hurricane events and restoration projects during the recent decades. Decreases in NDVI, SAVI, and FVC measured from Landsat images after hurricane events identified mangrove mortality that was directly related to damage from strong winds and storm surge. Modeled G values in the dwarf mangroves decreased from the 1990s to the 2000s indicating new growth and regrowth to areas around Taylor River in the coastal Everglades. Evapotranspiration remained relatively constant across all sites with the exception of SRS6 that exhibited higher ET rates following strong hurricanes. Minimum ET rates were found in the dwarf mangroves while maximum rates were obtained from the tall mangroves. There was also a decrease in soil heat flux and an increase in vegetation cover in the dwarf mangroves over time that was also accompanied by a rise in ET as a result of increases in biomass over the same period. Even though there are some limitations to the model related to estimating G compared to the measured value, the close comparisons from the other energy balance parameters suggest that there are other exports of energy from the environment from water and tidal transfers.

Additional Everglades-related restoration projects that are expected to affect both Shark and Taylor River have been completed or are planned to be completed, in the years after the last Landsat image in the present study. Continued monitoring through remote sensing can provide better regional understanding of how the mangrove environment responds to natural and anthropogenic intervention. Moreover, linking changes to the hydrogeological, meteorological and biophysical conditions in the coastal mangroves in

tropical and subtropical coastal wetlands are important for global water, energy and carbon budgets. The inclusion of older images from the long-term Landsat archive (1970s-2000s) and the new acquisitions from Landsat 8 as part of the Landsat Continuity Mission (2013-present) will undoubtedly provide crucial spatial and temporal diagnostics of changes to ET, the energy balance and biophysical conditions that may not be detected at the field-scale. Evapotranspiration and energy balance modeling in the coastal Everglades has the potential to be used in other similar environments throughout the Caribbean where data collection is minimal and could provide for better interpretations of the region.

3.8 References

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3.9 Tables

Table 3.1. Average values and standard deviations of fractional vegetation cover (*FVC*), net radiation (R_n), soil heat flux (G), sensible heat flux (H), latent heat flux (λE) and evapotranspiration (ET) for each site. The units for R_n , G , H and λE are in $W\ m^{-2}$ and in $mm\ day^{-1}$ for ET .

	Site	FVC x 100	R_n	G	H	λE	ET
Shark River	SRS4	90.4 ± 2.8	425.4 ± 27.5	129.2 ± 8.8	172.3 ± 13	160.5 ± 14.3	5.7 ± 0.5
	SRS-coast	64.4 ± 7.7	512.8 ± 25	174.6 ± 14.8	173.5 ± 13.1	175.5 ± 14.5	6.3 ± 0.5
	SRS6	83.9 ± 3.8	523.9 ± 26.2	139.9 ± 8	174.2 ± 13.3	218 ± 19.6	7.9 ± 0.7
Taylor River	TS6	16.4 ± 5.5	487.3 ± 33.8	227.4 ± 17.3	177.4 ± 13.9	104.4 ± 9.9	3.7 ± 0.3

Table 3.2. Analysis of Variance p -values for fractional vegetation cover (FVC), net radiation (R_n), soil heat flux (G) and latent heat (λE) as affected by site location and decade with respect to each site. Bold values indicate greater than 95% confidence

		n	FVC	R_n	G	λE
	Between sites	16	0.00	0.94	0.00	0.00
1990 v 2000	SRS4	8	0.76	0.31	0.046	0.79
	SRS6	8	0.76	0.63	0.84	0.90
	SRS-coast	8	0.20	0.56	0.13	0.16
	TS6	8	0.010	0.45	0.11	0.092

Table 3.3. Error analyses table for measured versus modeled values energy balance parameters at TS6 and SRS6. PFE= Percent Forecast Error; MAPE= Mean Absolute Percent Error; RMSE=Root Mean Square Error; NRMSE= Normalized RMSE; CVRMSE=Coefficient of Variation RMSE. Y_t are the measured values, F_t are the modeled values, Y_{t+1} , is the next forecasted value, Y_{avg} is the mean of the measured values, Y_{max} and Y_{min} are the maximum and minimum of the measured values, respectively, n is the number of samples and s_e is the standard error of the measured values.

Error Analysis	Formula	TS_Rn	SRS_Rn	SRS_G	SRS_H	SRS_ΔE	SRS6/TS6
PFE (%)	$(2 \times s_e / Y_{t+1}) \times 100$	13.0	11.6	21.6	15.6	19.5	11.6
MAPE (%)	$\Sigma(Y_t - F_t /Y_t)/n$	5.84	10.2	80.3	19.8	8.21	43.5
Nash-Sutcliffe	$\Sigma(Y_t - F_t)^2 / \Sigma(Y_t - Y_{avg})^2$	0.79	0.71	-12.6	-0.21	0.88	0.24
RMSE (W m ⁻²)	$\sqrt{\Sigma(Y_t - F_t)^2/n}$	55.0	53.0	11.8	46.4	29.4	64.1
NRMSE	$RMSE/(Y_{max} - Y_{min})$	11.5	13.8	8.55	29.6	12.2	18.5
Bias (W m ⁻²)	$\Sigma(Y_t - F_t)/n$	21.9	-26.0	113	-0.11	1.31	-155

Table 3.4. Satellite-derived and field-measured net radiation (R_n), soil heat flux (G), sensible heat flux (H), latent heat flux (λE) and evapotranspiration (ET) at SRS6 for each Landsat 5TM image acquisition. The units for R_n , G , H and λE are in W m^{-2} and in mm day^{-1} for ET.

Image Date	DOY	R_n		G		H		λE		ET	
		model	field	model	field	model	field	model	field	model	field
1/3/1997	3	391	349	121	17	132	68	137	128	4.9	4.6
1/20/2003	20	453	416	168	18	154	260	132	90	4.7	3.2
1/25/2005	25	433	492	136	36	147	137	150	149	5.4	5.4
1/31/2007	31	516	546	163	19	175	193	179	206	6.4	7.4
2/18/1996	49	483	524	152	24	164	184	168	162	6.0	5.8
2/26/1999	57	455	516	146	37	154	147	155	158	5.6	5.7
3/11/1998	71	528	597	170	27	179	237	179	173	6.4	6.2
3/21/1996	81	527	568	153	13	178	168	195	195	7.0	7.0
3/29/1993	89	579	616	130	41	174	184	275	283	9.9	10.2
4/1/1994	92	645	696	115	39	218	199	312	289	11.2	10.4
4/23/2008	114	713	705	113	46	241	185	358	287	13.7	10.3
5/4/2006	125	650	738	223	36	135	182	292	303	10.5	10.9
5/6/1995	127	696	749	118	31	236	222	343	351	12.3	12.6
10/11/2006	285	472	508	85	9	85	81	302	356	10.9	12.8
11/17/2008	323	512	397	145	14	173	99	194	220	7.4	7.9
11/20/2003	325	329	380	100	18	112	112	118	117	4.2	4.2
Average		523.9	549.9	139.9	26.6	166.0	166.1	218.0	216.7	7.9	7.8
S.D		108.6	127.8	33.1	11.5	41.7	55.1	81.3	84.3	3.0	3.0

3.10 Figures

Figure 3.1. Map showing the location of Florida (small inset), south Florida, Lake Okeechobee and Everglades National Park (large inset) and mangrove study sites in Everglades National Park.

Figure 3.2. Scatter plot of net radiation (R_n) recorded at the tower at in Shark River and R_n recorded at the tower in Taylor River.

Figure 3.3. Reflectance values of all visible and infrared Landsat bands and corrected surface temperature (Landsat Band 6) through time at dwarf mangrove site, (A) TS6 and tall mangroves, (B) SRS4 , (C) SRS-coast and (D) SRS6.

Figure 3.4. Plots of Landsat 5TM-derived spectral indices, Normalized Difference Vegetation Index, Fractional Vegetation Cover and Soil-Adjusted Vegetation Index at (A) TS6, (B) SRS4, (C) SRS-coast, and (D) SRS6. The grey and black dashed lines indicated the arithmetic mean for SAVI and FVC, respectively.

Figure 3.5. Multi-year average of net radiation (R_n), soil heat flux (G), sensible heat flux (H), latent heat of evaporation (λE) and Evapotranspiration (ET) for the 1990s and the 2000s for each site. Error bars denote 1 standard deviation.

Figure 3.6. Measured versus modeled scatter plots of (A) net radiation (R_n), (B) soil heat flux (G), (C) sensible heat flux (H) and (D) latent heat (λE). Grey dashed line represents a 1 to 1 ratio.

Figure 3.7. Satellite-based evapotranspiration (ET) rates in mm day^{-1} for each image acquisition at (A) TS6, (B) SRS-coast, (C) SRS4, and (D) SRS6.

Figure 3.8. Multi-annual average of evapotranspiration for the 1990s and 2000s for each site. Error bars denote 1 standard deviation.

Figure 3.9. (A) Scatter plots of net radiation (R_n) versus latent heat (λE) and (B) fractional vegetation cover (FVC) versus latent heat plots for each site.

Figure 3.10. Map of modeled latent heat (λE) values in the tall mangroves in southwestern Florida near Shark River in (A) post-tropical storm conditions (March 1993 acquisition) and in (B) steady-state conditions (November 2008). Trajectories of tropical storms are shown in Figure 10A. Mangrove study sites are marked with black diamonds.

Figure 3.11. Map of modeled latent heat (λE) values in the dwarf mangroves in southern Florida near Taylor River in (A) post-tropical storm conditions (March 1993 acquisition) and in (B) steady-state conditions (November 2008). Mangrove study sites are marked with black diamonds.

Figure 3.12. Map of path, trajectory and strength of tropical storms and hurricanes that have made landfall near the study sites between 1990 and 2009. The strength of storm at initial landfall is shown. Storms that are underlined were of particular interest.

CHAPTER 4: CONNECTING GROUNDWATER AND SURFACE WATER SOURCES IN A GROUNDWATER DEPENDENT COASTAL WETLAND: SIAN KA'AN BIOSPHERE RESERVE, QUINTANA ROO, MEXICO.

4.1 Abstract

Groundwater, pore water and surface water samples were collected in five different regions of the Sian Ka'an Biosphere Reserve (SKBR) along the eastern coast of the Yucatan Peninsula in Quintana Roo, Mexico. These samples were analyzed for major cations and anions, total phosphorus, total nitrogen, and stable isotopes of oxygen and hydrogen. Chemical modeling and a coupled principal component analysis and end-member mixing model were used to determine four water sources that discharge to the coastal wetlands and estuaries of the SKBR. Two chemically-distinct fresh ground water sources, sulfate-dominant water to the south and calcium-dominant water to the north, were found to contribute significantly to the coastal wetlands, estuaries and shallow coastal bay. In an anthropogenically-impacted northern estuary, surface water flow from the north was cut off by an elevated road, thereby creating hypersaline conditions and elevated nutrient concentrations in the groundwater south of the road. In a pristine estuary to the south, there was evidence of excess Ca^{2+} in the groundwater and surface water, greater than what was expected by typical freshwater-seawater mixing, most likely linked to carbonate dissolution (in the groundwater) and groundwater discharge to the surface water. Groundwater and pore water from a peten (tree island) in the southern estuary exhibited elevated phosphorus concentrations which may be an important contributor of this limiting nutrient to the estuaries. Lastly, the lower alkalinity measured in the surface water relative to the high-alkalinity groundwater, despite clear indication of groundwater discharge, suggests that inorganic carbon export through degassing of CO_2 could represent important carbon process in mangrove ecosystems. Our results demonstrate the importance of

groundwater discharge to estuaries and coasts in a karstic environment and the need for future investigations linking groundwater discharge and carbon processes.

4.2 Introduction

Karst systems are groundwater dependent ecosystems (GDE) that rely heavily on groundwater to maintain their structure and functionality (Murray et al., 2003; Eamus et al., 2006). The Yucatan peninsula is a highly karstified region that has limited surface water flow (Perry et al., 2003). Coastal wetlands are common environments along the coastline of the Yucatan and are important transition zones connecting terrestrial and aquatic GDEs that help to transfer material, energy and contaminants (Vervier et al., 2002). Alterations to the timing, quality, quantity and distribution of groundwater by natural or anthropogenic means can potentially alter both the form and function of the GDE, the coastal wetlands and the shallow coastal waters (Murray et al., 2003; Foster et al., 2003). Besides being an important driver and link for sustaining floral and faunal biodiversity in a wide variety of aquatic, terrestrial and coastal environments; GDEs and particularly wetlands provide a myriad of pecuniary ecosystem services for urban and agricultural development and expansion, recreation and other intangible benefits based upon social, cultural and ethical considerations (Foster and Chilton, 2003; Murray et al., 2003).

Coastal wetlands in karst regions can be heavily influenced by the timing and quality of groundwater delivered from upstream sources (Halse et al., 2003; Gondwe et al., 2011) and coastal groundwater discharge (Price et al., 2006). For instance, groundwater discharge in a coastal mangrove estuary in South Africa has been shown to persist through seasons of drought, contributing to the resilience of the estuary (Taylor et al., 2006). Additionally, groundwater has been shown to deliver nutrients, particularly phosphorus, to coastal mangroves in Brazil and Florida through coastal groundwater

discharge (Ovalle et al., 1990; Price et al., 2006). Groundwater levels and movement have also been shown to affect soil elevation (Whelan et al., 2005; Rogers and Saintilan, 2008), influence the exchange of material between tidal creek channels and interstitial water in the mangrove zone (Mazda and Ikeda, 2006), and contribute to coastal circulation (Kitheka, 1998).

Identifying subsurface water flow sources and pathways is important for understanding the links between GDEs and terrestrial and aquatic ecosystems (Cirimo and McDonnell, 1997). Various techniques (i.e., isotopic, chemical, and dye tracers) have been used to define water sources, measure water flow pathways, and quantify the contribution from each water source (Christophersen and Hooper, 1992; Doctor et al., 2006; Price et al., 2006). Natural geochemical tracers have been used in combination with a principle component analysis (PCA) and end-member mixing analysis have been used in a variety of GDEs such as mountain stream catchments (Hooper et al., 1990; Liu et al., 2004; Abesser et al., 2006); lowlands (Baker and Vervier, 2004; Garrett et al., 2012); wetlands (Vulava et al., 2008); and in karst terrains (Doctor et al., 2006).

A better understanding of the water flow pathways connecting GDEs is needed to help conserve and protect these important environments from the pressures of urban growth and development (Metcalf et al., 2010). In karst systems such as the Yucatan Peninsula, where there is little surface water flow but an intricate maze of caves, faults and fractures, groundwater becomes extremely important as well as difficult to study. Previous research has explored groundwater pathways in the geologically complex

region of the Yucatan peninsula (Perry et al., 2002; Marfia et al., 2004; Perry et al., 2009). The present study contributes to previous work conducted in the eastern Yucatan by investigating the interactions between the fresh groundwater sources in the peninsular interior and brackish and salt water sources located in the coastal mangrove zone and bay of the Sian Ka'an Biosphere Reserve (SKBR). The objectives of the present study was to 1) identify the various sources of water, particularly groundwater that discharge into the coastal wetlands and estuaries, and eventually to the Bahia de la Ascension; 2) quantify the proportion of each water source; and 3) compare the role of groundwater between pristine and disturbed mangrove sites.

4.3 Study Area

The Sian Ka'an Biosphere Reserve (SKBR) was established in 1986. Shortly thereafter, SKBR was declared a World Natural Heritage Site by UNESCO, was included on the RAMSAR List of Wetlands of International Importance and was the first project for the International Corporate Wetlands Restoration Partnership. At approximately 1.3 million acres (5280 km²), SKBR is the largest protected area in the Mexican Caribbean. The reserve is located on the eastern coast of the Yucatan peninsula, just south of the tourist destination of Tulum (Fig. 4.1). The reserve contains an extraordinary range of biodiversity as it encompasses the transition zone between upland tropical forests and savannas containing freshwater wetlands, lagoons and cenotes (sinkholes) with marine coral reefs via brackish coastal mangrove wetlands and estuaries, the largest of which is the Bahia de Ascension (Fig. 4.1). Coastal wetlands along the eastern boundary of the SKBR are composed of a mixture of mangrove communities ranging in structure from dwarf to tall forms that are primarily dominated by *Rhizophora mangle* (Adame et al.,

2013). Hummocks or petenes (tree islands) also occur in the freshwater and brackish water wetlands. These concentric formations tend to occur around cenotes, local term for sinkholes, and consist of tall hardwoods, palms or mangrove trees at the center radiating out to small trees, grasses or dwarf mangroves (Zaldívar-Jiménez et al., 2010).

Seasonal rains fall to the ground and then flow mostly underground through semi-deciduous forests, into an extensive freshwater-saltwater transitional wetland and ultimately, discharges into the Bahía de la Ascension. During the rainy season (mid-May-October), a majority of the annual rainfall (0.8-1.5 m) falls over the catchment (Olmstead and Duran, 1990). Evapotranspiration rates are poorly constrained in the area, but initial estimates range from 40-85% of the mean annual precipitation (Lesser, 1976; Beddows, 2004).

The Yucatan platform is ~150,000 km² and composed primarily of highly permeable limestone, ranging in thickness from ~1000 m along the northwest coast to ~150 m near the center of the peninsula (Ward et al., 1995). The carbonate platform is composed of a series of terraces, the oldest terrace (Eocene) is found in the center of the peninsula and the youngest (Holocene) formed along the coast (Richards and Richards, 2007). The high porosity and permeability of the limestone bedrock and the lack of soils allows water to quickly recharge the aquifer, resulting in the absence of surface streams (Beddows et al., 2007). Fractures, along with joints and bedding planes have been documented in nearby quarries and in flooded caverns and have created an extensive below ground cavernous pathway allowing increased hydraulic conductivity and

permeability (Beddows et al., 2007). Some dissolution features become exposed at the surface in the form of cenotes. The cenotes may extend ~100m below the water table and may connect with horizontal dissolution features associated with multiple sea-level stands (Beddows, 2004).

4.4 Methods

4.4.1 Peat Groundwater Wells

Groundwater wells were installed at six mangrove sites; two at Playon near the north end of the Bahia de Ascension and four along the Rio Negro near the southern end of the Bahia de Ascension (Fig. 4.1). The two wells at the Playon site were installed in December 2010 and placed on either side of a road that transects through the mangrove zone. These two sites were designated as SKP-1 (north of the road) and SKP-2 (south of the road) (Fig. 4.1 & 4.2) and were installed in the peat sediments just above the top of the bedrock at a depth of ~1 m. The well north of the road, SKP-1, was located in a relatively pristine, natural mangrove environment, while south of the road has experienced high tree mangrove mortality since the construction of the road (Fig. 4.2). The four wells constructed at the Rio Negro site (e.g., SKRN-0, SKRN-P, SKRN-1, and SKRN-2) were installed approximately 4-5 m from the river channel and located 5, 4, 3.2, and 1.5 km from the mouth of Rio Negro, respectively. Two wells, SKRN-1 and SKRN-2, were installed in December 2010 and wells, SKRN-0 and SKRN-P, were installed in May 2012. The groundwater well at SKRN-P was located within a tall mangrove peten (Adame et al. 2013), while the other 5 wells were installed amongst the dwarf mangroves. Each groundwater well was constructed from a 2.54 cm diameter

PVC pipe consisting of a solid riser and a 42.9 cm long well screen at the base. Wells were placed in the center of a 10.2 cm diameter borehole excavated with a bucket auger. Once wells were placed in the borehole, coarse sand was poured into the borehole surrounding the well screen to approximately 7.5 cm above the well screen. A 10-12 cm layer of fine sand was placed on top of the coarse sand and then followed by a layer of Portland cement up to the ground surface. Each well was developed 24 hours after installation by surging and pumping for at least one hour to remove any fine grained particulates that may have settled within the well and the coarse sand pack.

4.4.2 Water samples

Surface water samples were collected in and along the coastal mangrove region of the SKBR including the Bahia de la Ascension (BA) estuary, as well as from cenotes at Laguna Muyil located at the northern end of the SKBR, and Laguna Ocom located approximately 11 km south of the town of Felipe Carrillo Puerto (Fig. 4.1). Water samples were collected at Playon, Rio Negro, and the Bahia de la Ascension during the end of the wet season in December 2010. These coastal sites were resampled at the end of the dry season in May 2012 along with the two inland freshwater sites at Laguna Muyil and Ocom (Table 4.1 & 4.2). Groundwater samples (GW) were collected from the six well sites (e.g., SKRN-0, SKRN-1, SKRN-P, SKRN-2, SKP-1, SKP-2) located at Rio Negro and El Playon. Those groundwater wells were first purged of three well volumes of water using a peristaltic pump before the sample was collected. Pore water samples were collected at 20 cm (PW-20) and 50 cm (PW-50) below the ground surface at each well site using an acrylic tube and syringe. Surface water samples (SW) and GW samples were collected using a peristaltic pump.

Groundwater was also collected from a water supply well (PA-well) located approximately 8 km inland of the coastline along the Playon road (Fig. 4.1) and from a small village well (St. Isabel) located near Laguna Ocom. The PA-well was approximately 25 meters deep and bored into the limestone bedrock. Water from this well was sampled from a discharge valve in the well pipe after discharging for several minutes. The water from the well located at St. Isabel was sampled via a bucket that was lowered down the well and then filtered. The depth of the well was unknown; however, the water level in the well was approximately 8 meters below the ground surface.

Water temperature, specific conductance, dissolved oxygen and pH were measured in the field using an Orion multi-probe and a Thermo Scientific three-start pH meter at the time of sample collection. Water samples collected from each source (e.g., GW, PW-20, PW-50, and SW) consisted of a set of filtered and unfiltered samples. Unfiltered water samples were collected directly into dry, acid-washed bottles and acidified with a 10% HCl solution to be analyzed for total nutrient concentrations of phosphorus (TP), nitrogen (TN), and organic carbon (TOC). Water samples collected for ionic concentrations (cations, anions, and alkalinity) and stable isotopes were filtered through a 0.45 micron filter. Samples collected for cation analysis were acidified to a pH of less than 2 with 10% HCl. All samples were placed on ice and kept refrigerated until they were ready for analysis. Major anion (Cl^- and SO_4^{2-}) and cation (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) analyses were completed in the Hydrogeology Laboratory at FIU using a Dionex 120 Ion Chromatograph. Stable isotope ratios of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) were measured on a DLT-1000 Liquid Water Isotope Analyzer (Los Gatos, Inc.) with an accuracy of 0.6 and 0.2‰, respectively. Total Alkalinity was determined on the water

samples using a Brinkman Titrino 751 Titrator with 0.1N concentration of HCl to a pH of two. Total alkalinity was calculated from the mL of acid added at the inflection point closest to a pH of four. Change in volume of the sample due to the addition of the titrant was not considered. Total alkalinity was calculated as meq L^{-1} as HCO_3^- as the pH of the water samples was near neutral.

Saturation indices (S.I.) of the water samples were determined with respect to the minerals calcite, aragonite, dolomite, anhydrite and gypsum using the geochemical model PHREEQC version 2.14.2 (Parkhurst and Appelo, 1999). Positive S.I. values ($\text{S.I.} > 0$) indicated that the water sample was supersaturated with respect to that mineral and that mineral precipitation was most likely. Negative S.I. values ($\text{S.I.} < 0$) indicated undersaturated conditions with respect to that mineral and that mineral dissolution was most likely. Water samples with S.I. values near zero (± 0.05) were considered to be at saturation (or at equilibrium) with respect to that mineral, and neither precipitation nor dissolution was expected to predominate. In addition to the saturation indices, $\log p\text{CO}_2$ concentrations of the water samples were also determined using PHREEQC.

Total nutrient concentrations were determined at FIU's Southeast Environmental Research Center (SERC) water quality laboratory. Total phosphorus concentrations were determined using a dry ashing, acid hydrolysis technique developed by Solarzano and Sharp (1980). Total concentrations of nitrogen were analyzed on an ANTEK 7000N Nitrogen Analyzer that used O_2 as a carrier gas instead of argon to promote complete recovery of the nitrogen in the water samples (Frankovich and Jones, 1998). Total

organic carbon concentrations were measured by direct injection onto hot platinum catalysis in a Shimadzu TOC-5000 after first acidifying to a pH of less than 2 and purging with CO₂ free air.

4.4.3 Principal Component Analysis and End-Member Mixing Model

Two principle component analyses (PCA) were combined with an end-member analysis (EMMA) (Christophersen et al., 1990) to estimate the percent of the water contributed to each sample from a limited number of end-members. The alkalinity (HCO₃⁻), major anion (Cl⁻ and SO₄²⁻) and cation (Na⁺, K⁺, Mg²⁺, and Ca²⁺) concentration data from the groundwater, pore water, and surface water samples were used in one PCA. The other PCA utilized the same chemical constituents but without total alkalinity. The PCA used an orthogonal transformation to convert the water chemistry data into various principal components, where the majority of the variance was explained by the first two principal components, *U1* and *U2*. The eigenvectors of the *U1* and *U2* principal components made up the new transformed Euclidean space, *U*-space. Water source end-members were determined graphically by plotting the transformed data into *U*-space according to the methods described in Christophersen and Hooper (1992). Once the values of the end-members were identified, the proportions of each were determined by measuring the distance between each sample and each end-member in *U*-space using the EMMA as outlined in Christophersen and Hooper (1992). Lastly, the predicted ionic concentrations modeled by the joint PCA-EMMA were then compared with the measured ionic concentrations to determine the accuracy of the mixing model and to be sure the end-members were correctly identified. Further details and equations for the PCA and EMMA can be found in Christophersen and Hooper (1992).

4.5 Results

4.5.1 Water chemistry

Salinity of the samples at the Playon sites ranged from 0.3-53.2 psu in December 2010 and 4.3 to 76.9 psu in May 2012 (Table 4.1 & 4.2). The lowest salinity values were obtained in water samples from the potable well (PA-well) and from the surface water cenote (SW-2). The highest salinity at Playon was measured in the PW-50 sample at SKP-2. Salinity values in the disturbed mangroves (SKP-2; south side of the road) were about an order of magnitude greater than salinities in the undisturbed mangroves (SKP-1; north side of the road) (Table 4.1 & 4.2). In general, groundwater and pore water samples had higher salinities and lower pH values (<8) than surface water at both Playon sites.

Salinities at Rio Negro ranged from 1.1 to 22.1 psu in December 2010 and from 6.6 to 35.6 psu in May 2012 (Table 4.1 & 4.2). Surface water salinities increased along a gradient from the most inland site (SKRN-0) to the mouth of the Rio Negro (SKRN-2). The groundwater from SKRN-2, located closest to the bay, had the lowest salinity relative to the other Rio Negro sites (Table 4.1 & 4.2). The highest salinities (30-36 psu) were measured in the groundwater and porewater sample in the peten at SKRN-P. The pH values of the groundwater and pore water samples were below 7.5 while surface water pH was generally above 8. In addition, pH gradually increased from the upstream site, SKRN-0, to the downstream site, SKRN-2.

The salinity in the Bahia de la Ascension ranged from 22. to 31.4 psu in December 2010 and from 32.9 to 40.7 psu in May 2012 (Table 4.1 & 4.2). Water samples were collected from more locations in the Bahia de la Ascension in December 2010 as compared to May 2012, especially in the center of the bay; therefore, the range of salinity during the December 2010 may not be representative of the entire bay. The pH values of the water in the Bahia de la Ascension ranged between 8.26 and 8.58, with the lowest pH values often observed along the coastline (Table 4.1 & 4.2). Samples from the freshwater cenotes generally had salinities less than 1. Water temperatures were around 25-26°C for samples from cenotes (Sijil, Muyil Cenote1, and Muyil Cenote3) and relatively higher (>27°C) for local wells (St. Isabel) and lagoon (Laguna Ocom) (Table 4.1 & 4.2). Two samples from Laguna Ocom (Ocom and Ocom Cenote1) had higher pHs (>8.2) than the other freshwater samples (Table 4.1 & 4.2). These samples were obtained closer to the surface and at a distance away from the spring discharge.

The surface water samples collected in the Bahia de la Ascension clustered tightly on a piper diagram as sodium-chloride type water (Table 4.3 & 4.4; Fig. 4.3). The freshwater samples collected in the cenotes at Laguna Muyil and Laguna Ocom plotted in the center of the piper diagram with no particular dominant water type, but separate from one another with the Laguna Ocom samples containing slightly higher concentrations of sulfate (Fig. 4.3). Most of the groundwater, pore water, and surface water samples collected at Rio Negro and Playon were categorized as brackish water samples, defined as having a specific conductance greater than 5 mS cm⁻¹. The water samples from Rio Negro plotted on the piper diagram as a mixture of seawater and freshwater from

Laguna Ocom, while water samples from Playon plotted as a mixture of seawater and freshwater from Laguna Muyil.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the surface water from the Bahia de la Ascension ranged from +1.29‰ to +3.62‰ and from +7.69‰ to +14.78‰, respectively. Stable isotope values were more variable in the surface waters at Rio Negro and Playon, ranging from -0.86‰ to +6.16‰ for $\delta^{18}\text{O}$ and -3.47‰ to +28.16‰ for $\delta^2\text{H}$ (Table 4.1 & 4.2). Freshwater samples collected from the inland cenotes exhibited more depleted isotopic values with $\delta^{18}\text{O}$ values ranging from -5.17‰ to -1.78‰ and $\delta^2\text{H}$ values from -27.37‰ to -8.70‰. On a plot of $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ all of the brackish to saline water samples plotted below the meteoric water line (MWL) along an evaporation line with a slope of 4.9 while the freshwater cenote samples plotted on the MWL, with the exception of two samples (Fig. 4.4). These two freshwater cenote samples collected from the Laguna Ocom area (Laguna Ocom and Ocom Cenote1) had enriched values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, and plot higher along the evaporation line.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from the water samples collected at Rio Negro and the disturbed mangrove site at Playon (i.e., SKP-2) tended to become more negative with depth, while isotopic values at SKP-1 remained relatively consistent with depth (Table 4.1 & 4.2). Groundwater isotopic signatures averaged +1.07‰ ($\delta^{18}\text{O}$) and +0.92‰ ($\delta^2\text{H}$) at the Rio Negro sites and +1.90‰ ($\delta^{18}\text{O}$) and +8.96‰ ($\delta^2\text{H}$) at the Playon sites (Fig. 4.4). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the surface water averaged +4.82‰ and +22.84‰ at Rio Negro and +2.54‰ and +12.95‰ at Playon, respectively. Additionally, seasonal differences

were identified between the December 2010 samples and the May 2012 samples (Table 4.1 & 4.2). December 2010 samples from Rio Negro and Playon were more depleted (near zero for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$) than the subsequent samples collected in May 2012. Samples collected in the Bahia de la Ascension exhibited similar seasonal isotopic variability, with more depleted values from December 2010 (Table 4.1 & 4.2).

Total phosphorus concentrations were typically lowest in fresh groundwater and in the brackish and saline surface water samples (Fig. 4.5). Freshwater collected from the inland cenotes generally had TP concentrations, averaging $0.39 \mu\text{mol L}^{-1}$ at Laguna Ocom and $0.17 \mu\text{mol L}^{-1}$ (Fig. 4.5). Surface water TP concentrations in the brackish zone of Rio Negro and Playon ranged between 0.09 and $0.75 \mu\text{mol L}^{-1}$ and averaged $0.31 \mu\text{mol L}^{-1}$ (Table 4.5 & 4.6). Increasing surface water TP concentrations were observed along an estuarine gradient from Cl^- concentrations of ~ 15 to 200 mmol L^{-1} , followed by a decrease in TP concentration once Cl^- concentrations exceeded $\sim 300 \text{ mmol L}^{-1}$ (Fig. 4.6A). The TP concentrations in the Bahia de la Ascension were lower than the brackish surface water in Rio Negro and Playon, and ranged between 0.12 - $0.24 \mu\text{mol L}^{-1}$ with a mean concentration of $0.17 \mu\text{mol L}^{-1}$ (Fig. 4.5). Total phosphorus concentrations in the surface water at Rio Negro and Playon were on average 2-3 higher in May 2012 ($0.46 \mu\text{mol L}^{-1}$) than in December 2010 ($0.16 \mu\text{mol L}^{-1}$) (Table 4.5 & 4.6). The highest average TP concentrations were observed in the pore water and groundwater at Rio Negro and Playon (Table 4.5 & 4.6 & Fig. 4.5). In particular, subsurface samples from SKRN-P (peten site) at Rio Negro and SKP-2 (disturbed mangrove site) at Playon had TP concentrations that exceeded $1.6 \mu\text{mol L}^{-1}$ (Table 4.5 & 4.6).

The TN concentrations exhibited similar spatial variability as TP. Freshwater samples and surface water samples from the estuaries and Bahia de la Ascension tended to have lower TN concentrations. However, values were highly variable between the Laguna Ocom sites, with some of the lowest TN concentrations ($<50 \mu\text{mol L}^{-1}$) measured in the cenotes and the highest concentration ($919.54 \mu\text{mol L}^{-1}$) measured at the St. Isabel well (Table 4.5 & 4.6; Fig. 4.5). Groundwater and pore water samples generally had the highest average TN concentrations ranging from ~ 40 to $170 \mu\text{mol L}^{-1}$ (Table 4.5 & 4.6). Peak TN concentrations occurred in the subsurface samples at SKRN-P (peten site) and SKP-2 (disturbed mangrove sites) (Table 4.5 & 4.6; Fig. 4.6). Surface water TN concentrations followed a similar estuarine gradient as the TP concentrations, where the TN increased with increasing Cl^- concentrations from ~ 3 to 200 mmol L^{-1} followed by decreasing TN with Cl^- concentrations greater than 250 mmol L^{-1} (Fig. 4.6B).

Concentrations of TOC varied similarly as TP and TN between the water types (Fig. 4.5 & Fig. 4.6C). Likewise, the TOC concentrations varied with Cl^- concentrations; however, increases in TOC at lower Cl^- concentrations were not as pronounced as TP and TN (Fig. 4.6C). Water from the Bahia de la Ascension and the fresh groundwater from Laguna Ocom, and Laguna Muyil had the lowest TOC concentrations, ranging between 116 and 617 mmol L^{-1} (Table 4.5 & 4.6). Higher concentrations of TOC from the bay were observed in the December 2010 samples (Table 4.5 & 4.6). Pore water and groundwater, similar to TP and TN, had the highest concentrations of TOC ($>949 \text{ mmol L}^{-1}$) with concentrations 2-3 times higher at SKRN-P and SKP-2 (Fig. 4.6C).

The ratio of TN to TP (TN/TP) varied between water types (Fig. 4.5 & 4.6D). Surface water samples generally had the highest TN/TP ratios, ranging between ~150 -425 at the fresh groundwater sites (Laguna Ocom and Laguna Muyil) and between ~70-470 in all surface water samples collected amongst Rio Negro, Playon, and Bahia de la Ascension (Fig. 4.6D). Surface water collected during December 2010 at Rio Negro and Bahia de la Ascension had higher TN/TP ratios than those from May 2012. The average TN/TP ratios were lowest in pore water and groundwater samples collected in Rio Negro and Playon. There was an apparent decrease in TN/TP ratios with increasing Cl^- concentrations from ~15-250 mmol L^{-1} , followed by an increase in TN/TP ratio above Cl^- concentrations of ~300 mmol L^{-1} (Fig. 4.6D).

The PHREEQC model results indicated that all of the water samples were undersaturated with respect to gypsum and anhydrite, while most samples were at saturation or supersaturated with respect to calcite, aragonite, and dolomite (Table 4.7 & 4.8). Water samples from Laguna Muyil and Playon tended to be more undersaturated with respect to the evaporite minerals (gypsum and anhydrite) than the water samples from Laguna Ocom and Rio Negro (Table 4.7 & 4.8). For instance, saturation index values for gypsum and anhydrite were generally less than -2.3 and -1.5 for water samples collected at Laguna Muyil and Playon, respectively. Meanwhile, samples collected from Laguna Ocom and Rio Negro were slightly less undersaturated, with S.I. values greater than -2 at Laguna Ocom and greater than -1.5 at Rio Negro (Table 4.7 & 4.8). Only two samples collected from Laguna Muyil (i.e., Muyil Cenote1 and Laguna Muyil) were slightly undersaturated with respect to the carbonate minerals. Likewise, the groundwater samples collected at Playon in December 2010 were both undersaturated

or near equilibrium with respect to aragonite and calcite (Table 4.7 & 4.8). The log $p\text{CO}_2$ of surface water in the Bahia de la Ascension was close to current atmospheric concentrations ranging between -3.84 and -3.01 with a mean of -3.66. Pore water and groundwater samples had the highest log $p\text{CO}_2$ values ranging between -2.67 and -0.72 (Table 4.7 & 4.8). Fresh groundwater had moderate log $p\text{CO}_2$ values ranging between -3.07 to -1.71.

4.5.2 Water sources and principle component analysis

Various water sources were identified from the chemical constituents. Plots of Cl^- and SO_4^{2-} concentrations provided evidence of two distinct inland fresh water sources and a seawater end-member (Fig. 4.7A). Moreover, $\text{SO}_4^{2-}:\text{Cl}^-$ and $\text{Ca}^{2+}:\text{Na}^+$ ratios separated the water samples into similar end-members (Fig. 4.7B). Water samples collected around Laguna Ocom and Laguna Muyil separated out as the two freshwater end-members (Fig. 4.7). Laguna Muyil had Cl^- concentrations between 7.8-8.41 mmol L^{-1} and SO_4^{2-} concentrations between 0.4-0.43 mmol L^{-1} , while Laguna Ocom ranged between 0.3-6.0 mmol L^{-1} and 2.2-4.2 mmol L^{-1} , for Cl^- and SO_4^{2-} , respectively (Table 4.3 & 4.4; Fig. 4.7). The water from the St. Isabel well at Laguna Ocom had the lowest ionic concentrations and tended to plot by itself (Fig. 4.3 & 4.7). Similarly, Laguna Ocom also had higher $\text{SO}_4^{2-}:\text{Cl}^-$ ratios relative to Laguna Muyil and seawater samples (Fig. 4.7B). Water samples collected in the Bahia de la Ascension generally had the highest concentrations of ions but exhibited the lowest ratios of $\text{SO}_4^{2-}:\text{Cl}^-$ and $\text{Ca}^{2+}:\text{Na}^+$ (Fig. 4.7B). Water samples along the Rio Negro represented a mixture of freshwater from Laguna Ocom and the seawater from the bay. Water samples from Playon on the other hand, represented a mixture of freshwater from the north in Laguna Muyil with seawater

in from the bay (Fig. 4.1 & 7). Surface water samples collected at Playon and Rio Negro in December 2010 generally plotted closer to the freshwater end members. Subsurface samples (e.g., GW, PW-20 and PW-50) collected at SKP2, in the disturbed mangroves, plotted separately as the ionic concentrations were much higher than those found in seawater and indicated hypersaline (>40psu) conditions (Fig. 4.6 & 4.7).

The PCA utilized seven dissolved constituents (alkalinity, Cl^- , SO_4^{2+} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) and resulted in two principle components that comprised 97.3% of the variability of the water samples, *U1* (79.7%) and *U2* (17.6%) (Table 4.9). The first component, *U1*, made up 79.7% of the variability and was defined by Cl^- , SO_4^{2+} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . Meanwhile, the second component, *U2*, was defined by alkalinity and explained 17.6% of the variability (Table 4.9). Two end-members identified by the PCA were similar to the end-members defined earlier by the chemical analysis, seawater and freshwater; however, a third end-member was identified as peat groundwater (Fig. 4.8). Water from the Bahia de la Ascension plotted with the seawater end-member, as identified earlier by the ionic concentrations (Fig. 4.7 & 4.8). Laguna Muyil and Laguna Ocom samples clustered close together near the fresh water end-member. The peat groundwater end-member was identified by higher relative alkalinity and Ca^{2+} concentrations.

All surface water samples collected at Rio Negro and Playon plotted between the fresh water source and the seawater source, regardless of the time of year (Fig. 4.8). May 2012 surface water samples tended to plot closer to the seawater end-member and alternatively the December 2010 samples plotted closer to the fresh water end-member.

All subsurface samples (e.g., PW-20, PW-50, and GW) plotted above a mixing line connecting fresh water from Laguna Muyil and Laguna Ocom to seawater in the Bahia de la Ascension. These samples have higher relative concentrations of Ca^{2+} and alkalinity concentrations. The pore water and groundwater samples from the disturbed mangrove site at Playon (SKP-2) plotted outside and to the right of the three end-members because these samples had much higher ionic concentrations and were considered hypersaline with salinities in excess of 40 (Table 4.1 & 4.2; Fig. 4.8).

The second PCA, which involved all the ionic constituents except for alkalinity, exhibited similar patterns as the previous PCA with 97.7% of the variability being described by two principal components *U1* (91.4%) and *U2* (6.2%). The first two components represent the same chemical constituents as the first PCA analysis, but this time only Ca^{2+} comprised *U2* (Table 4.10). The same three end-members were identified, seawater, fresh groundwater, and peat groundwater; however, there was a more apparent peat groundwater end-member characterized by groundwater samples collected from SKRN-P (peten) (Fig. 4.9).

The surface water samples in the second PCA from Rio Negro and Playon, once again, plotted between the fresh groundwater and seawater end-members; however, these samples also exhibited mixing associated with the peat groundwater end-member (Fig. 4.9). Water samples collected from the undisturbed mangrove site at Playon (SKP-1) tended to plot closer to the freshwater end-member. Meanwhile, samples from Rio Negro plotted in the center of all three end-members. A seasonal signal was also

observed in the surface water at Rio Negro whereby samples collected in December 2010 plotted closer to the fresh groundwater end-member and the May 2012 samples tended to plot as a mix of all three end-members (Fig. 4.9).

Contributions from each end-member were determined for all of the water samples using the PCA without alkalinity (Fig. 4.10). Samples plotting closer to the end-members had higher contributions from that particular end-member. Water samples from the Bahia de la Ascension generally contained greater than 80% of seawater with the remaining fraction composed of freshwater (Fig. 4.10). Sampling locations near the mouth of Rio Negro (e.g., SK-81, SK-82) exhibited the greatest fluctuation between sampling periods in the amount of freshwater contained in the samples (Fig. 4.10). Surface water samples at Rio Negro from December 2010 had freshwater end-member contributions ranging between 35% at the mouth (SK-82) to over 95% in the upper reaches of the river (SKRN-0) (Fig. 4.10). Fresh water contributed between ~60-90% at SKP-1, but had little to no contribution at SKP-2 (Fig. 4.10). Surface water samples collected from Rio Negro in December 2010 contained little peat groundwater; however, the May 2012 samples composed of 10-20% peat groundwater (Fig. 4.10). There was little contribution of peat groundwater to samples from Playon, regardless of the collection date. The peten site in Rio Negro (SKRN-P) had the highest contribution of peat groundwater, comprising 80-100% of the samples.

4.6 Discussion

4.6.1 End-member mixing

Two distinct fresh water sources were identified from the water samples collected from in and around Sian Ka'an. The water collected in the cenotes near Laguna Ocom contained elevated concentrations of SO_4^{2-} and exhibited higher $\text{SO}_4^{2-}:\text{Cl}^-$ ratios when compared to the cenotes of Laguna Muyil (Fig. 4.6). The water chemistry from Laguna Muyil is characterized as a calcium-bicarbonate type water with little to no sulfate indicative of water in contact with limestone. Saturation indices calculated using PHREEQC indicate that all of the water samples collected during this study were saturated or near-saturated with respect to calcite and aragonite except for two samples at Laguna Muyil that were slightly undersaturated (Table 4.7 & 4.8). The inland waters of Laguna Muyil may be more representative of recharge water that has not had time to reach equilibrium with respect to the carbonate minerals calcite and aragonite. The persistent undersaturation with respect to gypsum and anhydrite of all of the water samples collected in this study is similar to other studies in the region (Perry et al., 2002) (Table 4.7 & 4.8) and indicates that the groundwater in the region has not been able to equilibrate with those minerals.

An areally extensive impact breccia containing limestones, silicates and evaporite sequences has been identified in the central and southeastern portion of the state of Quintana Roo as a result of the Chixulub impact (Perry et al., 2003; Lefticariu et al., 2006). The evaporite material is primarily composed of the sulfate-rich minerals anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), both of which have higher solubility than

calcite or aragonite. Water samples collected from groundwater wells, cenotes and lakes in surrounding sites to the west and to the south, in a region known to contain an evaporite sequence, have been shown to contain elevated SO_4^{2-} concentrations relative to water samples collected in more northern areas of the peninsula (Perry et al., 1995; Perry et al., 2002). The boundary and depth of the evaporite sequence has not yet been fully constrained because of the poor consolidation of the geologic material that has led some studies to recognize various areas as impact ejecta (Pope et al., 2005) or Holocene alluvium (Salinas-Prieto et al., 2007). However, recent microscopic analyses and Sr^+ isotopic data has further constrained the evaporite region and identified locally breached perched water tables from dissolution evaporates and Albion Formation (Perry et al., 2002). The cenotes around Laguna Ocom are most likely hydrologically connected to the sulfate-rich evaporite layers.

The differentiation in water chemistry between the two fresh water sources, Laguna Muyil and Laguna Ocom, suggest a hydraulic divide between the two regions (Fig. 4.2 & 6). Groundwater flows in the Yucatan have been mapped by a number of researchers and are reviewed in Bauer-Gottwein et al. (2011). The ionic water chemistry data indicates a clear connection between surface water along Rio Negro and freshwater around Laguna Ocom and is consistent with an eastward groundwater flow that has been mapped in the region west of Laguna Ocom (Bauer-Gottwein et al., 2011). The groundwater flow paths of the Yucatan are reviewed by Bauer-Gottwein et al (2011), where multiple groundwater pathways have been mapped from the central peninsula to the coast as well as northwestward from northern Belize to Tulum. However, the chemistry between Laguna Muyil and Laguna Ocom, measured in this study, does not

indicate any mixing between the two freshwater end-members. Therefore, the northwestward groundwater pathway previously measured may be part of another hydrogeologic section that is not in contact with evaporite sequences in the Albion formation as suggested by Perry et al, (2009) and could flow through northeast-southwest trending fractures and faults suggested by Gondwe et al, (2010).

Oxygen isotopic values, $\delta^{18}\text{O}$, from the freshwater cenotes Laguna Ocom and Laguna Muyil ($-5.17\text{‰} > \delta^{18}\text{O} > -1.78\text{‰}$) are very similar to $\delta^{18}\text{O}$ values of rainfall measured in the Yucatan at Merida (-1.5‰ ; Perry et al., 2003) and Celestun [-2.9‰ ; Stalker et al (accepted in Estuaries and Coasts)]; and in nearby Veracruz and San Salvador (-4.0 and -6.5‰ , respectively; Lachniet and Patterson, 2009) and south Florida ($-3.6\text{‰} > \delta^{18}\text{O} > -2.8\text{‰}$; Price et al., 2006). The freshwater in the cenotes is expected to flow through the groundwater system and discharge to the surface water upstream of SKRN-O and SKP-1 at Rio Negro and Playon, respectively. Once the fresh groundwater discharges to the surface it undergoes evaporation and mixes with water from the Bahia de la Ascension, thereby increasing the isotopic values along the evaporation and seawater mixing lines on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ plot (Fig. 4.3). Heavier $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were measured in the upstream reaches of Rio Negro (SKRN-0) relative to the mouth (SKRN-2) possibly suggesting longer transit times in the upper reaches of the river. Freshwater may also discharge at other localities along Rio Negro, as suggested by the greater freshwater contribution in the groundwater at SKRN-2 (Fig. 4.8). Lateral discharge from the river banks could also contribute to the surface water (Santos et al., 2010); however, there is very little contribution of peat groundwater to the surface water (Fig. 4.8).

4.6.2 Nutrient dynamics

The estuarine zone of the SKBR can be characterized as an oligotrophic-mesotrophic system as a result of the low nutrient concentrations in the surface water (Nurnberg, 1996) similar to other environments in the Yucatan (Chelum lagoon; Herrera- Silveira et al., 2002), Belize (Rejmánková and Komárkova, 2000) and south Florida (Childers et al., 2006). The relatively low TP concentrations and high TN:TP ratios measured in this study suggest that the SKBR is a phosphorus-limited system, typical of other carbonate-rich environments (Short et al., 1990; Fourqurean et al., 1992; Jensen et al., 1998; Rejmánková and Komárkova, 2000). Surface water TN and TP concentrations at Rio Negro and Playon were very similar to the concentrations measured in the surface waters of the southeastern Everglades, where concentrations range between ~25-100 $\mu\text{mol L}^{-1}$ for TN and ~0.2-1.5 $\mu\text{mol L}^{-1}$ for TP (Childers et al., 2006). Total phosphorus concentrations in the coastal SKBR exhibit analogous spatial variability as the “upside down” nature of the Florida Coastal Everglades in which the limiting nutrient (i.e., TP) supply originates from a marine source (Childers et al., 2006). The lower nutrient concentrations in the surface water of Rio Negro and Playon and the Bahia de la Ascension suggest that nitrogen and phosphorus maybe removed from the water column quickly via biological processes, phosphorus adsorption to carbonate sediments, or redox processes.

The oligotrophic-mesotrophic nature of SKBR differs from mesotrophic-eutrophic lagoonal estuaries found along the northwestern coast (Celestun and Dzilam lagoons; Herrera- Silveira et al., 2002), northern coast (Ria Largatos; Valdes and Real, 2004) and eastern coast of the Yucatan (Mutcheler et al., 2007). Anthropogenic activity is one of

the major factors, in addition to longer residence times of the surface water that have contributed to the higher nutrient concentrations in the coastal lagoons (Medina-Gomez and Herrera-Silveira, 2003; Herrera-Silveira et al., 2004). However, the SKBR and vicinity are more segregated from the anthropogenic pressures from the northwest and northeast Yucatan and the surface waters in the SKBR exhibited phosphorus limited conditions during both sampling periods. Recent trends in tourism development and urbanization encroaching on the northern boundary of the SKBR could push the reserve into more mesotrophic to eutrophic conditions in the near future.

Groundwater and pore water samples had elevated nutrient concentrations relative to the overriding surface water. Among the groundwater and pore water, the samples collected from the disturbed mangrove area (SKP-2) had TP concentrations an order of magnitude higher than the other samples, save a groundwater sample at SKRN-P and SKP-1 (Fig. 4.5). The elevated TP concentrations may have been a result of the release of phosphorus from the dissolution of calcium carbonate; however, there would be an accompanied increase in calcium concentrations above what would be conserved by mixing with seawater. A slight excess in Ca^{2+} was observed at SKP-2, with concentrations that plotted just above the freshwater-seawater conservative mixing line (Fig. 4.9). The lack of mangrove vegetation at SKP-2 and the hypersaline condition suggests that a heterotrophic environment exceeds that of autotrophy which increases the oxidation of organic matter, and in turn dissolves calcium carbonate (Fourquaran et al., 2012). However, the dissolution of calcium carbonate might not be as strong as that from SKRN-P, because Ca^{2+} concentrations measured in the subsurface as SKP-2 plot above, but closer, to the freshwater-seawater conservative mixing line (Fig. 4.11).

Additionally, higher salinities greater than 9 have been shown to have a propensity to release more Ca-bound phosphorus in carbonate-rich sediments in Florida Bay (Zhang and Huang, 2011). Alternatively, the high TP concentration in the groundwater at SKRN-P was associated with elevated Ca^{2+} concentrations with respect to the freshwater-seawater conservative mixing line and may suggest that there is groundwater discharge to the surface water around the peten at SKRN-P (Fig. 4.5 & 4.10). The increased phosphorus in the peten may also be a result of the release of phosphorus from the marine sediments that were found at the base of the groundwater well or from the breakdown of organic matter. The highest TP concentrations measured in the surface water during the dry season were obtained near SKRN-P and SKRN-1 and could be sourced by the possible coastal groundwater discharge around the nearby peten, as many petens are known to contain groundwater springs (Adame et al., 2013). Lastly, the PCA without alkalinity indicated that the surface water collected at Rio Negro in May 2012 contained 10-20% of peat groundwater (Fig. 4.10).

4.6.3 Groundwater/surface water disconnect in disturbed mangrove zone.

The water from the two sites at Playon exhibit two distinct chemical signatures despite being only a few meters apart. The site north of the road, SKP-1 is derived primarily from a freshwater source similar to the water at Laguna Muyil while SKP-2 is characterized as evaporated seawater with little to no contribution of freshwater (Fig. 4.6 & 4.10). The primary reason for the chemical dichotomy between these two nearby sites is the hydraulic barrier created by the slightly elevated (~1 m above the marsh surface) dirt road separating the two sites. The road essentially cuts off surface water runoff from the north causing it to be dammed north of the dirt road. The higher freshwater head levels

north of the road allow for more infiltration of the surface water into the subsurface sediments. The low peat groundwater signal (<20%) that is characterized by elevated Ca^{2+} and alkalinity may also suggest faster infiltration and lower residence times, inhibiting the decomposition of organic matter that leads to increased alkalinity. A small culvert in the road does not allow for sufficient water exchange between the north and south side of the road. The isotopic and ionic chemistry from the water at SKP-2 suggests that seawater from the Bahia de la Ascension entered the area through tidal propagation and then evaporated within the basin causing hypersaline conditions. Mangroves on the north side of the road at Playon were observed to be in more productive and healthier conditions than the hypersaline environment to the south.

4.6.4 Groundwater chemistry and groundwater discharge

Elevated concentrations of Ca^{2+} have been used as an indicator for brackish groundwater discharge (Price et al., 2006). Concentrations of Ca^{2+} above what were expected from conservative mixing of freshwater and seawater were observed in the surface water samples at Rio Negro (Fig. 4.11). The additional source of Ca^{2+} observed in the samples most likely comes from the dissolution of the limestone bedrock and carbonate sediments at the interface between fresh groundwater and intruding seawater as seen in other regions of the Yucatan (Back et al., 1986), the Bahamas (Smart et al., 1988) and in south Florida (Price et al., 2006). The brackish groundwater mixing zone can become undersaturated with respect to calcite and aragonite even though both end-members may be saturated (Wigley and Plummer, 1976; Sanford and Konikow, 1989; Rezaei et al., 2005). Only a few subsurface samples were collected in Rio Negro and Playon that

exhibited undersaturation with respect to calcite and aragonite; however, many of the subsurface samples were at or just above S.I. values (Table 4.7 & 4.8).

Petens studied in the SKBR were found to have the highest carbon stocks and were associated with freshwater springs (Adame et al., 2013). The pore water and groundwater collected in the peten located at SKRN-P had little contribution from the fresh groundwater end-member (<18%) or from seawater (<8%) (Fig.10). The small contribution of fresh groundwater and seawater at SKRN-P was in contrast to groundwater collected at the other three groundwater sites along Rio Negro that contained a 30-60% fresh groundwater signal (Fig. 4.10). The alkalinity in the subsurface peten samples was similar to other subsurface samples collected in Rio Negro and Playon (Table 4.3 & 4.4), as well as other similar sites in the Florida Everglades (Xapata, 2010), Australia (Maher et al., 2013), and the Dominican Republic (Sherman et al., 1998). However, the peten samples were distinctly different than the other samples in Rio Negro because of the elevated Ca^{2+} concentrations (Table 4.3 & 4.4; Fig. 4.9). The higher Ca^{2+} concentrations at SKRN-P suggest there may be slightly more dissolution of calcite and aragonite as a result of higher $\log p\text{CO}_2$ concentrations and corresponding lower pH values associated with the breakdown of organic matter and mangrove root respiration in the subsurface (Bouillon et al., 2008).

The complex karst geology and the preferential flow through the below ground cave network and faults and fractures may control the location and extent of the coastal groundwater discharge zone. Groundwater at the upstream stream site in Rio Negro,

SKRN-0, contained approximately 20% seawater while SKRN-1 and SKRN-2 showed no signs of seawater. One suggestion for the low seawater component in the groundwater could be coastal groundwater discharge from two different aquifer sources. A perched and regional aquifer have been identified in areas inland of Rio Negro (Perry et al., 2009) with more dynamic groundwater level changes and higher pressure heads in the perched aquifer (Gondwe et al., 2010). Coastal groundwater discharge in the peten could be sourced from a deeper aquifer than may have breached the aquitard; separating the two aquifers either by dissolution or from fracturing and faulting (Gondwe, et al., 2010) while the perched aquifer containing fresher water may be able to reach the coast. The lack of research and understanding of the coastal geology in the SKBR make these results difficult to interpret and further hydrogeochemical and resistivity studies are needed to constrain the local geology.

Water samples collected in the subsurface also contained higher alkalinity relative to the surface water (Table 4.3 & 4.4). These elevated concentrations have been measured in the pore water and groundwater of similar mangrove environments and are a result of sulfate reduction (Ovalle et al., 1990), carbonate dissolution (Middelburg et al., 1996) or the addition of CO₂ through autotrophic and heterotrophic respiration (Bouillon et al., 2008). Zapata and Price (2010) and Lagomasino et al., (submitted manuscript) measured high alkalinity and TP in the groundwater and pore water of a dwarf mangrove ecosystem in southwestern Everglades. In addition, brackish groundwater discharge was recorded during the late dry season in the southwestern Everglades (Zapata and Price, 2010). The higher alkalinity measured in the pore water and groundwater sites at Rio Negro, in conjunction with the elevated Ca²⁺ and TP concentrations measured in the

surface water and groundwater at Rio Negro strongly suggest that coastal groundwater discharge occurs (Price et al., 2006) ~5 km inland around SKRN-P, despite the fact that the surface water alkalinity was an order of magnitude less than the groundwater (Table 4.3 & 4.4). Groundwater discharge could be associated with seepage from the peat into the surface water from tidal pumping (Maher et al., 2013) or from deeper brackish groundwater discharge associated with the mixing zone between freshwater and seawater intrusion (Price et al 2006). The combination of groundwater discharge and the discrepancy between alkalinity values between the groundwater and surface water could represent an important dissolved inorganic carbon pathway in Sian Ka'an, and other similar mangrove wetlands like the southern Everglades.

The differences in alkalinity between the groundwater and surface water are also mirrored in the log $p\text{CO}_2$ values of the two water types (Table 4.7 & 4.8). In the surface water, log $p\text{CO}_2$ was comparable to current atmospheric conditions (-3.8), whereas groundwater samples in the peat and cenotes tended be 1-2 orders of magnitude higher suggesting increases of CO_2 from autotrophic and heterotrophic respiration (Bouillon et al., 2008). The PCA that included alkalinity suggested that there was little to no interaction between the groundwater and surface water, which was in contrast to the Ca^{2+} and TP concentrations indicating a connection between the two waters. However, the PCA without alkalinity indicated a clear signal of peat groundwater mixing with surface water at Rio Negro (Fig. 4.9 & 4.10). This discrepancy of the loss of alkalinity between the groundwater and surface water was most likely caused by the evasion (outgassing) of CO_2 as the groundwater discharges to the surface water, which can reach equilibrium in the matter of minutes (Moran, 2010). When the high alkalinity, low

pH groundwater discharges to the surface water, the CO₂ gas quickly escapes from the surface water to the atmosphere. Moran (2010) showed that when the influent CO₂ concentrations were high (>25 mg L⁻¹) the amount of CO₂ degassed from the system varied with salinity where 75% of CO₂ was degassed for seawater and 87% for freshwater. This exchange and release of carbon could be substantial because 10-20% of the surface water at Rio Negro is composed of the peat groundwater end-member (Fig. 4.10). In their review, Bouillon et al (2008) discusses the “missing” carbon in mangrove forests and hypothesizes inorganic carbon through CO₂ degassing could help to close the carbon budget. More recently, Maher et al., (2013), suggested that groundwater advection through tidal pumping exported 93-99% of dissolved inorganic carbon and were an order of magnitude greater than organic carbon exports.

4.7 Conclusions

Using differences in aqueous geochemistry and natural chemical tracers in the groundwater and surface water we were able to discern two distinct upland fresh groundwater sources that contribute water to the SKBR: one water source that is sulfate-rich identified in the Laguna Ocom region and another source that is calcium-rich identified at Laguna Muyil. Water passing through Laguna Ocom discharges into Rio Negro; however, it is not certain whether water from Laguna Muyil feeds directly into Playon. There is strong evidence from chemical and multivariate analyses that water at both Playon and Laguna Muyil originate from a similar source. Fresh groundwater from Laguna Ocom was found to be rich in sulfate and most likely caused by dissolution of the calcium-sulfate minerals anhydrite and gypsum which are common to an evaporite layer in the regional subsurface. Fresh groundwater from Laguna Muyil exhibited a

calcium carbonate type chemical signature typical for water-rock interactions with limestones. Three major sources of water were identified as contributing to the coastal region of SKBR; fresh groundwater, peat groundwater and seawater. The peat groundwater end-member was observed in pore water and groundwater samples at Rio Negro and Playon, but with affinity to the downstream sites at Rio Negro (SKRN-P, SKRN-1, SKRN-2). The occurrence of a dirt road at Playon was found to inhibit the exchange of freshwater from the north with seawater from the south. As a result, hypersaline conditions exist south of the road leading to an absence in mangroves and a buildup of nutrients in the subsurface peats. Nutrient and chemical analyses indicate that the SKBR is an oligotrophic-mesotrophic environment with phosphorus limitations, but were less P-limited in the surface water brackish zone between 200-350 mmol L⁻¹ of Cl⁻, similar to the southeastern Everglades. The highest nutrient concentrations were found in the pore water and groundwater, and more specifically, in the disturbed mangrove site, SKP-2, and the peten site, SKRN-P. The combination of high alkalinity and high nutrient content in the subsurface discharging to the low alkalinity, low nutrient surface water at Rio Negro demonstrates the importance of this process in water and inorganic carbon exchange. Identifying individual water sources and their mixtures are important in understanding the fate and transport of groundwater as it passes through the ecosystem. Changes to the groundwater hydrology caused by natural events and/or exacerbated by increased development, water demands, or waste-water disposal could result in changes to the water chemistry and ecology of the put pressure on the coastal wetlands of the SKBR as well as shallow seagrass and coral reef coastal communities.

4.8 References

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4.9 Tables

Table 4.1. Summary of field parameters and stable isotopes for water sampling sites during the end of the wet season, from December 7-9, 2010.

Site	Station name	Water type	Temp (°C)	Conductivity (mS)	Salinity (psu)	pH	δD	δ ¹⁸ O
Bahia de la Ascension	SKRN-82	SW	23.7	35.14	22.1	8.36	0.71	-0.12
	SKP-109	SW	23.8	48.19	31.4	8.32	7.69	1.29
	SKP-110	SW	24.6	45.34	24.6	*	*	*
	SKP-111	SW	23.6	45.15	29.3	8.41	6.95	0.24
	SK-lagoon	SW	25.5	37.95	24.1	8.35	14.65	2.06
Playon	PA-well	GW	25.3	1.303	0.6	7.62	-22.37	-4.32
	SKP-1	SW	24.9	5	2.7	7.8	5.70	0.25
	SKP-1	GW	24	10.48	5.9	6.55	1.54	-0.25
	SKP-2	GW	25.3	76.6	53.2	6.62	11.20	2.02
	SKP-2	SW	29.4	19.83	11.7	*	*	*
	SW-2	SW	21.7	0	0.3	7.36	-7.77	-1.71

Site	Station name	Water type	Temp (°C)	Conductivity (mS)	Salinity (psu)	pH	δD	δ ¹⁸ O
Rio Negro	SKRN-0	SW	20.8	2.606	1.4	7.62	0.67	0.15
	SKRN-1	GW	27.9	31.87	19.8	6.57	-0.08	-0.78
	SKRN-1	SW	23.7	2.46	1.3	7.92	-0.25	-0.25
	SKRN-2	SW	24.1	3.97	2.1	8.07	-0.93	-0.86
	SKRN-20	SW	23.9	2.838	1.5	8.07	-3.47	-0.16
	SKRN-81	SW	23.7	9.88	5.5	8.13	1.55	0.36
	SKRN-P1	SW	22.1	11.54	6.6	7.24	N.S.	N.S.

Table 4.2. Summary of field parameters and stable isotopes for water sampling sites during the end of the dry season, from May 5-9, 2012.

Site	Station name	Water type	Temp (°C)	Conductivity (mS)	Salinity (psu)	pH	δD	δ ¹⁸ O
Bahia de la Ascension	SK-82	SW	30	57.7	38.3	8.56	13.59	2.96
	SK-109	SW	29.3	55.3	36.7	8.26	14.48	3.08
	SK-111	SW	30.8	55.9	37	8.58	14.72	2.86
	SK-117	SW	30.9	58.2	38.7	8.57	6.54	1.98
	SK-118	SW	30.1	54.5	36	8.58	10.13	2.06
	SK-124	SW	29.8	50.4	32.9	8.56	12.73	2.71
	SK-126	SW	29.9	57	37.8	8.42	10.07	1.57
	SK-127	SW	29.5	52.7	34.6	8.33	10.34	1.77
	SK-128	SW	29.4	55	36.3	8.27	12.34	1.54
	SK-129	SW	30	56.5	37.4	8.47	12.38	3.62
	SK-130	SW	29.9	55.5	35.2	8.54	14.11	3.37
	SK-131	SW	30.1	53.6	35.3	8.48	15.81	3.40
	SK-Lagoon	SW	33.2	61.4	40.7	8.32		
Playon	SKP-1	SW	29	8.49	4.3	7.99	2.96	1.09
	SKP-1	20	30.1	9.97	5.6	7.48	4.19	1.29
	SKP-1	50	31.7	20.49	12.1	7.33	6.75	1.32
	SKP-1	GW	30.2	14.41	8.3	7.61	8.87	1.69
	SKP-2	SW	31.9	55.9	36.9	8.55	22.93	4.00
	SKP-2	20	32	78.6	54.5	7.11	15.36	2.40
	SKP-2	50	31	105	76.9	6.99	9.86	1.79
	SKP-2	GW	30.2	99.5	71.9	7.2	9.04	2.11

Site	Station name	Water type	Temp (°C)	Conductivity (mS)	Salinity (psu)	pH	δD	δ ¹⁸ O
Rio Negro	SKRN-0	SW	29.5	16.84	9.8	7.97	28.16	6.16
	SKRN-0	20	31.1	17.63	10.7	7.36	21.89	4.26
	SKRN-0	50	29.7	22.33	13.3	6.84	-4.17	0.47
	SKRN-0	GW	29.6	25.45	15.5	6.9	2.51	1.45
	SKRN-P	SW	30.9	22.01	13.2	8.13	20.88	4.66
	SKRN-P	20	27.6	39.97	25.5	6.45	6.23	0.53
	SKRN-P	50	28	43.37	27.5	6.47	-2.93	-0.56
	SKRN-P	GW	27.2	50.6	33	6.47	-3.53	-0.37
	SKRN-P cenote	SW	30.1	47.4	30.9	7.96	*	*
	SKRN-P cenote	20	28.4	51	33.3	6.83	*	*
	SKRN-P cenote	50	28.5	54	35.6	6.51	*	*
	SKRN-1	SW	32.4	29.05	17.7	8.15	20.02	3.93
	SKRN-1	20	34.1	14.7	20	7.06	19.51	3.61
	SKRN-1	50	30.6	14.56	20	6.91	13.65	2.80
	SKRN-1	GW	29.2	34.07	21.3	6.86	-0.67	0.69
	SKRN-2	SW	34.4	37.55	23.5	8.44	20.36	4.38
	SKRN-2	20	30.6	17.81	25	7.34	11.59	2.08
	SKRN-2	50	31.5	30.39	18.8	7.11		
	SKRN-2	GW	29.1	11.65	6.6	6.84		

Site	Station name	Water type	Temp (°C)	Conductivity (mS)	Salinity (psu)	pH	δD	δ ¹⁸ O
Laguna Ocom	Laguna Ocom	SW	29.4	15.4	0.8	8.26	9.69	2.82
	St Isabel	GW	27.8	0.61	0.3	7.38	-22.45	-3.13
	Balam Nah	GW	27.5	2.288	1.2	7.34	*	*
	Siiijil	Cenote	26.5	1.745	0.9	7.03	-27.37	-5.17
	Cenote1	Cenote	30.9	1.282	0.6	8.39	13.49	4.25
Laguna Muyil	Muyil Cenote1	Cenote	25.8	1.732	0.9	7.2	-24.63	-4.54
	Muyil Cenote2	Cenote	26	1.73	0.9	7.25	*	*
	Muyil Cenote3	Cenote	25.5	1.73	0.9	7.32		
	Laguna Muyil	SW	*	*	0.7	*	-8.70	-1.78

Table 4.3. Summary of alkalinity and major cations and anions for water sampling sites during the end of the wet season, from December 7-9, 2010.

Site	Station name	Water type	Alkalinity	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Bahia de la Ascension	SKRN-82	SW	2.7	348.4	6.9	292.7	8.0	35.6	7.8
	SKP-109	SW	2.8	478.7	9.2	415.5	11.3	50.7	9.2
	SKP-111	SW	3.4	438.4	9.1	388.1	10.7	47.8	8.5
	SK-lagoon	SW	5.0	346.8	7.0	322.1	8.1	37.8	7.8
Playon	PA-well	GW	4.4	7.9	0.2	6.0	0.1	0.8	2.1
	SKP-1	SW	6.1	44.4	0.5	33.7	0.7	3.8	2.2
	SKP-1	GW	7.4	99.3	1.5	77.0	1.8	9.5	3.7
	SKP-2	GW	10.7	863.4	19.9	708.5	13.1	102.8	17.0
	SW-2	SW	4.3	2.3	0.0	1.6	0.0	0.2	1.5
Rio Negro	SKRN-0	SW	4.1	15.4	1.3	12.8	0.3	3.2	3.1
	SKRN-1	GW	19.4	314.4	6.0	262.8	6.3	35.9	14.2
	SKRN-1	SW	3.0	16.1	1.4	12.0	0.3	3.1	2.8
	SKRN-2	SW	3.1	32.2	1.5	23.9	0.5	4.3	2.9
	SKRN-20	SW	3.8	18.7	1.3	15.8	0.4	3.4	2.9
	SKRN-81	SW	3.0	82.1	2.4	72.0	2.0	9.9	4.1

Table 4.4. Summary of alkalinity and major cations and anions for water sampling sites during the end of the dry season, from May 5-9, 2012.

Site	Station name	Water type	Alkalinity	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Bahia de la Ascension	SK-82	SW	2.4	583.0	29.3	510.5	13.1	62.6	11.0
	SK-109	SW	2.7	539.1	27.3	473.7	10.4	56.0	10.3
	SK-111	SW	2.4	600.6	30.0	475.7	11.1	56.6	10.2
	SK-117	SW	2.4	497.2	23.5	481.0	12.0	55.5	10.9
	SK-118	SW	2.6	553.5	27.4	464.6	10.8	55.6	10.1
	SK-124	SW	2.5	478.6	24.5	423.5	9.8	49.5	10.5
	SK-126	SW	2.8	573.6	28.8	486.9	11.4	58.0	10.4
	SK-127	SW	2.7	544.7	27.6	446.3	10.4	53.4	9.8
	SK-128	SW	2.7	591.5	29.6	470.7	11.0	56.4	10.4
	SK-129	SW	2.4	615.7	30.7	478.8	10.4	57.4	10.3
	SK-130	SW	2.5	464.4	24.0	452.6	10.6	54.1	10.0
	SK-131	SW	2.8	586.6	28.0	453.8	10.6	54.2	9.9
	SK-Lagoon	SW	3.0	631.5	32.8	520.2	11.8	61.9	12.0
Playon	SKP-1	SW	4.5	72.3	3.2	56.7	1.2	6.6	3.9
	SKP-1	20	5.0	89.6	4.0	73.5	1.6	8.7	4.5
	SKP-1	50	9.0	229.8	10.4	205.0	5.0	27.1	8.9
	SKP-1	GW	5.3	141.6	7.0	114.3	2.6	13.7	5.4
	SKP-2	SW	3.4	396.1	21.8	481.5	12.7	57.3	13.0
	SKP-2	20	5.6	857.6	49.5	759.5	15.0	102.3	20.8
	SKP-2	50	9.3	1110.3	65.3	957.9	21.1	131.0	22.8
	SKP-2	GW	7.9	1043.1	61.7	892.1	19.5	114.5	23.4

Site	Station name	Water type	Alkalinity	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Rio Negro	SKRN-0	SW	3.5	142.7	12.6	125.8	2.8	17.8	8.1
	SKRN-0	20	6.6	158.9	12.0	142.7	3.1	19.4	9.0
	SKRN-0	50	11.6	227.8	14.9	186.3	4.0	26.0	14.0
	SKRN-0	GW	10.8	247.5	15.8	203.9	4.7	27.6	12.7
	SKRN-P	SW	3.3	207.8	15.2	176.0	3.9	23.0	8.4
	SKRN-P	20	11.2	430.9	32.7	344.4	6.5	49.8	21.8
	SKRN-P	50	13.5	456.5	36.8	361.8	8.2	54.0	24.2
	SKRN-P	GW	16.4	549.8	38.6	420.0	7.3	60.8	27.1
	SKRN-1	SW	3.2	225.9	14.6	201.7	6.0	25.7	7.9
	SKRN-1	20	5.2	262.2	15.8	240.4	5.4	30.7	10.4
	SKRN-1	50	8.0	256.0	15.5	233.1	5.1	30.6	11.0
	SKRN-1	GW	17.3	317.9	16.1	277.0	5.9	37.2	14.8
	SKRN-2	SW	3.0	368.6	21.4	307.1	8.2	38.8	11.0
	SKRN-2	20	8.9	354.0	20.2	292.0	6.4	37.5	13.1
	SKRN-2	50	17.7	294.5	13.2	252.8	6.2	34.8	11.9
	SKRN-2	GW	10.6	96.0	7.8	84.1	2.3	11.7	9.9

Site	Station name	Water type	Alkalinity	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Laguna Ocom	Laguna Ocom	SW	2.9	6.0	3.1	6.3	0.2	2.4	2.1
	St Isabel	GW	4.8	0.3	0.1	0.4	0.0	0.2	2.6
	Sijil	Cenote	7.0	3.7	4.2	4.3	0.1	2.5	5.0
	Cenote1	Cenote	7.3	3.2	2.2	6.8	0.1	1.4	3.3
Laguna Muyil	Muyil Cenote1	Cenote	3.1	8.4	0.4	3.5	0.1	1.7	2.3
	Muyil Cenote3	Cenote	7.3	8.4	0.4	7.1	0.1	1.6	3.5
	Laguna Muyil	SW	3.3	7.8	0.4	6.4	0.1	1.5	1.2

Table 4.5. Summary of nutrient concentrations for water sampling sites during the end of the wet season, from December 7-9, 2010.

Site	Station name	Water type	TN (uM)	TP (uM)	TOC (uM)
Bahia de la Ascension	SKRN-82	SW	39.32	0.15	538.92
	SKP-109	SW	30.80	0.12	412.50
	SKP-111	SW	43.09	0.12	565.67
	SK-lagoon	SW	83.09	0.37	1187.50
Playon	PA-well	GW	22.37	0.13	278.08
	SKP-1	SW	45.96	0.14	1168.33
	SKP-1	GW	85.87	0.58	1622.50
	SKP-2	GW	204.44	1.60	2032.50
	SW-2	SW	51.94	0.35	1672.50
Rio Negro	SKRN-0	SW	36.51	0.10	749.50
	SKRN-1	GW	64.94	0.32	1920.83
	SKRN-1	SW	38.42	0.10	730.17
	SKRN-2	SW	41.05	0.11	847.50
	SKRN-20	SW	43.33	0.09	825.75
	SKRN-81	SW	66.89	0.19	809.42

Table 4.6. Summary of nutrient concentrations for water sampling sites during the end of the dry season, from May 5-9, 2010.

Site	Station name	Water type	TN (uM)	TP (uM)	TOC (uM)
Bahia De Ascension	SK-82	SW	26.95	0.23	301.17
	SK-109	SW	30.39	0.18	356.83
	SK-111	SW	29.81	0.18	307.00
	SK-117	SW	16.40	0.15	195.80
	SK-118	SW	25.49	0.15	320.17
	SK-124	SW	41.83	0.18	561.33
	SK-126	SW	22.22	0.18	240.50
	SK-127	SW	18.93	0.24	303.00
	SK-128	SW	29.90	0.15	310.67
	SK-129	SW	25.62	0.22	279.50
	SK-130	SW	28.77	0.15	372.17
	SK-131	SW	24.83	0.19	319.17
	SK-Lagoon	SW	86.53	0.34	1179.00
Playon	SKP-1	SW	50.02	0.28	1789.67
	SKP-1	20	83.53	0.47	1809.00
	SKP-1	50	142.18	1.67	3705.67
	SKP-1	GW	94.09	0.64	2102.33
	SKP-2	SW	128.75	0.32	2254.00
	SKP-2	20	336.33	1.65	3500.83
	SKP-2	50	580.89	4.53	3089.17
	SKP-2	GW	502.50	3.02	2967.50

Site	Station name	Water type	TN (uM)	TP (uM)	TOC (uM)
Rio Negro	SKRN-0	SW	86.14	0.38	1678.00
	SKRN-0	GW	76.01	0.85	1409.67
	SKRN-P	SW	96.98	0.55	1497.33
	SKRN-P	GW	168.01	6.72	4564.67
	SKRN-1	SW	52.90	0.75	1040.00
	SKRN-1	GW	78.26	0.76	1921.00
	SKRN-2	SW	80.18	0.57	1452.33
	SKRN-2	GW	21.63	0.29	262.57
Laguna Ocom	Laguna Ocom	SW	31.13	0.14	412.50
	St Isabel	GW	919.54	0.56	96.13
	Sijjil	Cenote	127.07	0.49	120.93
	Cenote1	Cenote	81.44	0.53	119.00
Laguna Muyil	Muyil Cenote1	Cenote	28.25	0.16	617.67
	Muyil Cenote3	Cenote	119.31	0.28	116.17
	Laguna Muyil	SW	50.70	0.23	295.67

Table 4.7. Summary of saturation indices for major karst minerals and the log of pCO₂ for water samples collected from December 7-9, 2010.

Date	Site	Type	Sample Name	Charge Balance	Gypsum	Anhydrite	Aragonite	Calcite	Dolomite	CO2(g)
Dec-2010	Bahia de la Ascension	SW	SKP-109	4.84E-02	-1.13	-1.33	0.76	0.9	2.74	-3.42
Dec-2010		SW	SKP-111	5.29E-02	-1.14	-1.35	0.89	1.04	3	-3.44
Dec-2010		SW	SKRN-81	1.20E-02	-1.5	-1.72	0.61	0.75	2.03	-3.01
Dec-2010		SW	SKRN-82	2.30E-02	-1.21	-1.41	0.77	0.91	2.65	-3.45
Dec-2010	Playon	GW	PA-well	-8.23E-04	-2.45	-2.67	0.3	0.44	0.6	-2.22
Dec-2010		SW	SK-lagoon	5.70E-02	-1.22	-1.43	1.02	1.16	3.18	-3.17
Dec-2010		SW	SKP-1	-5.09E-03	-2.24	-2.45	0.47	0.61	1.59	-2.31
Dec-2010		GW	SKP-1	-4.81E-03	-1.76	-1.98	-0.6	-0.46	-0.35	-1
Dec-2010		GW	SKP-2	5.03E-02	-0.72	-0.91	-0.06	0.08	1.15	-1.1
Dec-2010	Rio Negro	SW	SKRN-0	3.39E-03	-1.54	-1.75	0.33	0.47	1.09	-2.28
Dec-2010		GW	SKRN-1	2.38E-02	-1.02	-1.23	0.19	0.33	1.23	-0.69
Dec-2010		SW	SKRN-1	2.40E-03	-1.54	-1.75	0.45	0.6	1.37	-2.73
Dec-2010		SW	SKRN-2	6.94E-04	-1.6	-1.82	0.58	0.72	1.75	-2.88
Dec-2010		SW	SKRN-20	3.67E-03	-1.6	-1.82	0.69	0.83	1.88	-2.78

Table 4.8 Summary of saturation indices for major karst minerals and the log of pCO₂ for water samples collected from May 5-9, 2012.

Date	Site	Type	Sample Name	Charge Balance	Gypsum	Anhydrite	Aragonite	Calcite	Dolomite	CO2(g)
May-2012	Bahia de la Ascension	SW	SK-82	6.83E-02	-1.08	-1.28	0.9	1.04	3.03	-3.83
May-2012		SW	SK-109	5.86E-02	-1.12	-1.32	0.73	0.88	2.67	-3.37
May-2012		SW	SK-111	-2.48E-03	-1.08	-1.29	0.91	1.05	3.03	-3.84
May-2012		SW	SK-117	1.41E-01	-1.18	-1.39	0.9	1.04	3.03	-3.84
May-2012		SW	SK-118	3.39E-02	-1.12	-1.32	0.93	1.08	3.08	-3.81
May-2012		SW	SK-124	5.78E-02	-1.12	-1.32	0.93	1.08	3.01	-3.79
May-2012		SW	SK-126	4.09E-02	-1.1	-1.3	0.86	1.01	2.95	-3.57
May-2012		SW	SK-127	1.79E-02	-1.12	-1.32	0.77	0.92	2.76	-3.45
May-2012		SW	SK-128	1.47E-03	-1.08	-1.28	0.75	0.89	2.7	-3.38
May-2012		SW	SK-129	-1.45E-02	-1.07	-1.28	0.83	0.97	2.88	-3.69
May-2012	Laguna Muiil	Cenote	Muyil Cenote1	-2.22E-04	-2.47	-2.69	-0.24	-0.1	-0.18	-1.96
May-2012		Cenote	Muyil Cenote3	1.42E-03	-2.34	-2.56	0.4	0.54	0.89	-1.71
May-2012		Cenote	Laguna Muiil	5.65E-04	-2.72	-2.94	-0.68	-0.53	-0.81	-1.72
May-2012	Laguna Ocom	Cenote	Ocum	4.44E-03	-1.7	-1.92	0.69	0.83	1.87	-3.07
May-2012		Cenote	St Isabel	1.09E-03	-2.95	-3.17	0.26	0.4	-0.26	-1.94
May-2012		Cenote	Sijil	5.96E-03	-1.28	-1.5	0.21	0.36	0.54	-1.45
May-2012		Cenote	Cenote1	5.70E-03	-1.65	-1.87	1.41	1.55	2.91	-2.82

Date	Site	Type	Sample Name	Charge Balance	Gypsum	Anhydrite	Aragonite	Calcite	Dolomite	CO2(g)
May-2012	Rio Negro	20	SKRN-0	2.94E-02	-1.18	-1.39	0.42	0.57	1.63	-1.91
May-2012		20	SKRN-P	3.12E-02	-0.68	-0.89	-0.03	0.11	0.76	-0.84
May-2012		20	SKRN-1	5.09E-02	-1.15	-1.36	0.01	0.15	0.94	-1.74
May-2012		20	SKRN-2	2.38E-02	-1.02	-1.23	0.58	0.72	2.07	-1.81
May-2012		50	SKRN-0	2.13E-02	-1	-1.22	0.28	0.42	1.28	-1.17
May-2012		50	SKRN-P	3.29E-02	-0.61	-0.81	0.1	0.24	1.01	-0.79
May-2012		50	SKRN-1	4.81E-02	-1.13	-1.34	0.07	0.21	1.04	-1.41
May-2012		50	SKRN-2	3.19E-02	-1.21	-1.42	0.62	0.76	2.16	-1.27
May-2012		GW	SKRN-0	2.08E-02	-1.04	-1.25	0.26	0.4	1.31	-1.26
May-2012		GW	SKRN-P	1.17E-02	-0.58	-0.79	0.21	0.36	1.25	-0.72
May-2012		GW	SKRN-1	4.18E-02	-1.06	-1.27	0.44	0.59	1.74	-1.04
May-2012		GW	SKRN-2	1.78E-02	-1.19	-1.41	0.22	0.37	0.96	-1.16
May-2012		SW	SKRN-0	2.59E-02	-1.16	-1.38	0.71	0.85	2.2	-2.81
May-2012		SW	SKRN-P	2.19E-02	-1.16	-1.37	0.78	0.92	2.45	-3.05
May-2012		SW	SKRN-1	1.01E-01	-1.28	-1.5	0.78	0.92	2.52	-3.1
May-2012		SW	SKRN-2	3.00E-02	-1.07	-1.28	1.01	1.15	3.02	-3.51
May-2012	Playon	SW	SKP-1	-6.65E-06	-1.79	-2.01	0.68	0.82	2.01	-2.67
May-2012		20	SKP-1	4.36E-03	-1.7	-1.92	0.26	0.4	1.23	-2.11
May-2012		50	SKP-1	3.68E-02	-1.35	-1.56	0.47	0.61	1.87	-1.77
May-2012		GW	SKP-1	3.84E-03	-1.53	-1.74	0.4	0.55	1.65	-2.24
May-2012		SW	SKP-2	6.65E-01			1.15	1.29	3.42	-3.69
May-2012		20	SKP-2	1.04E+00			0.22	0.37	1.62	-1.9
May-2012		50	SKP-2	1.31E+00			0.32	0.47	1.89	-1.59
May-2012		GW	SKP-2	1.21E+00			0.48	0.63	2.14	-1.86

Table 4.9. Results of two principal component analysis (with alkalinity) shown as factor loadings for all principal components with the percent variability associated with each principal component.

Parameter	Principal Components						
	U1	U2	U3	U4	U5	U6	U7
Alkalinity	0.16	0.97	-0.16	0.01	0.00	0.00	0.00
Cl ⁻	0.99	-0.12	-0.06	0.03	-0.04	0.07	-0.01
SO ₄ ²⁻	0.99	-0.01	0.06	0.15	-0.03	-0.04	0.01
Na ⁺	0.99	-0.14	-0.06	-0.04	0.05	0.01	0.02
K ⁺	0.96	-0.21	-0.11	-0.11	-0.05	-0.04	0.00
Mg ²⁺	0.99	-0.07	-0.04	0.03	0.07	-0.01	-0.02
Ca ²⁺	0.85	0.45	0.27	-0.07	0.00	0.01	0.00
Variability (%)	79.74	17.57	1.76	0.62	0.18	0.12	0.01
Cumulative %	79.74	97.31	99.07	99.69	99.87	99.99	100.00

Table 4.10. Results of principal component analysis (without alkalinity) shown as factor loadings for all principal components with the percent variability associated with each principal component.

Parameter	Principal Components					
	U1	U2	U3	U4	U5	U6
Cl ⁻	0.99	-0.12	-0.02	-0.07	0.07	-0.01
SO ₄ ²⁻	0.95	0.13	0.28	0.01	-0.01	0.00
Na ⁺	0.99	-0.15	-0.04	-0.01	-0.02	0.03
K ⁺	0.96	-0.23	-0.05	0.13	0.01	-0.01
Mg ²⁺	0.99	-0.08	-0.06	-0.07	-0.06	-0.02
Ca ²⁺	0.85	0.51	-0.12	0.02	0.01	0.00
Variability (%)	91.44	6.25	1.70	0.45	0.14	0.02
Cumulative %	91.44	97.69	99.39	99.84	99.98	100.00

4.10 Figures

Figure 4.1. (A) Map of the Sian Ka'an Biosphere Reserve showing the locations of study sites in the Bahia de la Ascension. False color composite Landsat 5 Thematic Mapper images for (B) Laguna Muyil, (C) Playon, (D) Rio Negro, (E) and Laguna Ocom.

Figure 4.2. Picture, facing west, of Playon showing the undisturbed mangrove site (SKP-1) to the right (north) of the road, and the disturbed mangrove site (SKP-2) to the left (south) of the road.

Figure 4.3. Piper diagram showing major ion chemistry of water samples collected in the Bahia de la Ascension, Laguna Ocom, Playon, Rio Negro, and Laguna Muyil.

Figure 4.4. Plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for water samples collected at each site in the Sian Ka'an Biosphere reserve. The global meteoric water line (GMWL) is plotted as a grey line. The local evaporation line is plotted as a dotted black line.

Figure 4.5. Bar charts of average (± 1 standard deviation) total nitrogen (TN), total phosphorus (TP) and TN:TP ratios plotted for samples from Bahia de la Ascension, Laguna Muyil, Laguna Muyil, brackish surface water from Playon and Rio Negro, pore water and groundwater.

Figure 4.6. Semi-log plots of chloride concentration versus (A) total phosphorus concentrations, (B) total nitrogen, (C) total organic carbon, and (D) TN:TP ratios from all samples collected in the Sian Ka'an Biosphere Reserve. Outlying samples from sites SKRN-P (peten) and SKP-2 (disturbed mangroves) are circled in black.

Figure 4.7. Log-log plots of (A) chloride (Cl^-) versus sulfate (SO_4^{2-}) concentrations and (B) $\text{Cl}^-/\text{SO}_4^{2-}$ versus $\text{Ca}^{2+}/\text{Na}^+$ sodium ratios for all water samples collected in the Sian Ka'an Biosphere Reserve.

Figure 4.8. Water chemistry data from the Sian Ka'an Biosphere Reserve plotted in U-space as defined by the orthogonal projections from the principal component analysis. Recognized end-members are shown; Fresh groundwater, seawater, and peat groundwater. Outlying samples from SKP-2 (disturbed mangroves) are circled in black.

Figure 4.9. Principal component plot (without alkalinity) for water chemistry data from the Sian Ka'an Biosphere Reserve plotted in U-space as defined by the orthogonal projections from the principal component analysis. Recognized end-members are shown; Fresh groundwater, seawater, and peat groundwater. Outlying samples from SKP-2 (disturbed mangroves) are circled in black.

Figure 4.10. Stacked bar chart indicating the percentage of each end member, fresh groundwater (blue), seawater (orange), and peat groundwater (green) calculated for each water sample using the end-member mixing model.

Figure 4.11. Plot of chloride versus calcium concentrations from water samples collected in the Sian Ka'an Biosphere Reserve. A conservative freshwater-seawater mixing line is plotted as a black line. Samples above the line indicate excess calcium.

CHAPTER 5: SUMMARY AND CONCLUSIONS

This dissertation explored various processes related to the ecohydrology and hydrogeochemistry of two mangrove wetlands in Everglades National Park (U.S.A.) and the Sian Ka'an Biosphere Reserve (Mexico), each with similar bedrock geology, meteorology, and nutrient patterns. With growing concerns of climate change, sea-level rise, population growth, and urban development, tropical and subtropical wetland coastlines are susceptible to degradation and eutrophication. Mangroves, in particular, provide many tangible and intangible ecosystem services needed for maintaining biodiversity, cultural significance, and water supply and quality. The Everglades and Sian Ka'an provided two environments on a spectrum of anthropogenic intervention. The Everglades has been primarily impacted by decades of water diversion and retention, and more recently, by restoration efforts all while being on the cusp of a large, ever-expanding metropolis. The Sian Ka'an Biosphere Reserve is bordered by rural, but developing, municipalities and has remained relatively untouched by humans.

Research conducted in the Everglades and Sian Ka'an employed a combination of water chemistry data (e.g., major anions, cations, and nutrients, and stable isotopes), leaf-scale reflectance, optical satellite imagery and multivariate analysis. The combination of these different chemical, spectral, and statistical approaches provided more information about the local and regional variability in water chemistry, surface energy and evapotranspiration, and groundwater movement through coastal carbonate wetlands.

The major findings from Chapter 2 provided us with field and satellite-based biophysical spectral responses for tall and dwarf mangrove varieties along the southern Everglades. Changes to the mangrove leaf spectral responses were correlated with surface and subsurface ionic and nutrient concentrations. Near-infrared reflectance values among red mangroves tended to be lower when subsurface ionic concentrations were high and when nutrient concentrations were low. Similarly, spectral data collected by the Landsat 5TM satellite had comparable relationships to water chemistry as did the leaf-level data. Building upon those relationships, Landsat imagery was able to successfully estimate the dry season variability of surface water chloride concentrations across the southern Everglades, regardless of the mangrove species or the variety (i.e., tall vs. dwarf).

In Chapter 3, satellite imagery was used to recognize the effects of natural disturbances and human intervention has on the spectral response, surface energy and evapotranspiration of mangroves in the Everglades. The results indicated that fractional vegetation cover and soil heat flux were more variable through time at mangrove sites that were hydrologically more stagnant with limited tidal flushing. These biophysically stressed conditions resulted in lower evapotranspiration rates within basin-type mangroves, particularly in the dwarf mangroves. Meanwhile, mangroves located along larger tidal creeks tended to have more stable reflectance properties over time and more resilient after hurricane events. Evapotranspiration rates were generally highest in the tall mangroves closer to the Gulf of Mexico. Lastly, evapotranspiration at mangroves along the tidal channels was closely linked with changes in net radiation, while the fractional vegetation cover was more predictive of evapotranspiration in irregularly flooded mangrove areas.

Groundwater and surface water interactions in the Sian Ka'an Biosphere Reserve were investigated in Chapter 4. The Reserve is essentially devoid of major surface water bodies within the interior portions of the peninsula because of the highly karstified bedrock, making the coastal wetlands reliant on groundwater flow. Groundwater and surface water sample data from various regions around the Reserve were applied to chemical and multivariate models and indicated that there were two chemically distinct fresh groundwater sources. Each groundwater source discharged exclusively into one of two separate estuaries located on opposite sides of the Bahia de la Ascension. Low nutrient concentrations measured in the surface waters connoted that the fresh groundwater and estuarine and bay surface water were all phosphorus-limited. Brackish coastal groundwater discharge was suggested to up-estuary because of the occurrence of elevated phosphorus and calcium concentrations. The highest nutrient concentrations were found in the porewater and groundwater of a peten and in an area of disturbed mangroves; however, these high concentrations occur because of different process. Groundwater discharge was responsible for phosphorus concentrations in the peten, and heterotrophy and hypersalinization were responsible for the concentrations in the disturbed mangroves.

Further investigations of ecohydrologic processes between marine sourced and groundwater sourced phosphorous additions are needed to better constrain the effects of the timing, location, and amount of nutrient loading. Additional experiments relating various biophysical stressors to diurnal spectral measurements of soil and leaf properties could provide better insight for measuring and estimating water chemistry, water levels, surface energy and evapotranspiration. These observations will allow for

improved spectral unmixing of satellite data. Moreover, understanding the spectral response to the landscape measured by satellites offers the incentive of cost-effective method to remotely collect site and regional data without the expense of multiple field expeditions. Many of the Caribbean islands have similar geological, meteorological, ecological processes as those from Sian Ka'an and the Everglades. Expanding research to other carbonate mangrove ecosystems that have been impacted and saved from anthropogenic alterations, like those previously mentioned, will be extremely useful for future restoration and mitigation efforts, and ensure the health and vigor of coastal ecosystem for decades and centuries to come.

APPENDICES

Appendix A. Guidelines for authors on the referencing style of each of the journal that Chapters 2, 3, and 4 were submitted to.

CHAPTER 2: ESTIMATING MAJOR ION AND NUTRIENT CONCENTRATIONS IN MANGROVE ESTUARIES IN EVERGLADES NATIONAL PARK USING LEAF AND SATELLITE REFLECTANCE (Submitted to Remote Sensing of Environment)

References should be cited in the text by the name(s) of the author(s), followed by the year of publication in parentheses, e.g., Baret and Guyot (1991). When the same author and year are cited again, these references should have the year followed by (a), (b), etc. The reference list should be typed alphabetically, according to the following examples:

Journal: Baret, F., & Guyot, G. (1991). Potentials and limits of vegetation indices for LAI and APAR assessment. *Remote Sensing of Environment*, 35, 161-173

Book: Schott, J.R. (1997). *Remote Sensing: The Image Chain Approach*. (pp. 52-62). New York: Oxford University Press

Edited Book: Kaufman, Y.J. (1989). The atmospheric effect on remote sensing and its corrections. In G. Asrar (Ed.), *Theory and Applications of Optical Remote Sensing* (pp. 336-428). New York: Wiley

Theses, and Other Work: Style as a journal article with as much source information as possible.

CHAPTER 3: SPATIAL AND TEMPORAL VARIABILITY IN SPECTRAL-BASED SURFACE ENERGY AND EVAPOTRANSPIRATION MEASURED FROM LANDSAT 5TM ACROSS TWO MANGROVE ECOTONES (Submitted to Agricultural and Forest Meteorology)

There are no strict requirements on reference formatting at submission. References can be in any style or format as long as the style is consistent. Where applicable, author(s) name(s), journal title/book title, chapter title/article title, year of publication, volume number/book chapter and the pagination must be present. Use of DOI is highly encouraged.

CHAPTER 4: CONNECTING GROUNDWATER AND SURFACE WATER SOURCES IN A GROUNDWATER DEPENDENT COASTAL WETLAND: SIAN KA'AN BIOSPHERE RESERVE, QUINTANA ROO, MEXICO (To be submitted to Limnology and Oceanography)

Journal: Fenchel, T. 1986. Protozoan filter feeding. *Prog. Protistol.* 1: 65-113.

Articles with a Digital Object Identifier (DOI): Many older papers that were originally published with page numbers have been retroactively assigned DOI's while some newer electronic journals assign article identifiers instead of page numbers (HTML being the primary form of publication). Thus, a paper with a DOI may contain page numbers, an article identifier, or both, and at least one of these is needed to complete the reference.

De Pol-Holz, R., O. Ulloa, L. Dezileau, J. Kaiser, F. Lamy, and D. Hebbeln. 2006. Melting of the patagonian ice sheet and deglacial perturbations of the nitrogen cycle in the eastern South Pacific. *Geophys. Res. Lett.* 33: L04704, doi:10.1029/2005GL024477

Check that every DOI that you cite is correct via the [doi system website](#). Note that references with a doi *do not* have a period at the end; this facilitates electronic lookup (doi's terminated with a period fail when sent to doi resolver websites).

Book: Stumm, W., and J. Morgan. 1981. Aquatic chemistry, 2nd ed. Wiley.

Chapter: Codispoti, L. A. 1983. Nitrogen in upwelling systems, p. 513-564. *In* E. J. Carpenter and D. G. Capone [eds.], Nitrogen in the marine environment. Academic.

Thesis: Kimmance, S. A. 2001. The interactive effect of temperature and food concentration on plankton grazing and growth rates. Ph.D. thesis. Univ. of Liverpool.

For abbreviations of journal names refer to [Chemical Abstracts Service Source Index \(CASSI\)](#) or [Biosis](#).

Appendix B. Study site latitude and longitude coordinates.

SITE	STATION	LATITUDE (N)	LONGITUDE (W)
Playon	SKP-1	19.8229	-87.4989
	SKP-2	19.8225	-87.4985
Rio Negro	SKRN-0	19.4870	-87.7077
	SKRN-P	19.4866	-87.7009
	SKRN-1	19.4898	-87.6953
	SKRN-2	19.4966	-87.6804
Bahia de la Ascension	SK-82	19.5849	-87.6243
	SK-109	19.8002	-87.5189
	SK-111	19.8153	-87.4895
	SK-117	19.6037	-87.5481
	SK-118	19.7551	-87.4944
	SK-124	19.6001	-87.6796
	SK-126	19.6441	-87.6351
	SK-127	19.7094	-87.6197
	SK-128	19.7687	-87.5850
	SK-129	19.6400	-87.5738
	SK-130	19.7057	-87.5614
	SK-131	19.7564	-87.5272
Laguna Ocom	Laguna Ocom	19.4660	-88.1043
	St Isabel	19.4696	-88.0985
	Balam Nah	19.4766	-88.0668
	Sijil	19.4746	-88.0515
	Cenote 1	19.4706	-88.0293
Laguna Muyil	Muyil Cenote1	20.0785	-87.6095
	Muyil Cenote2	20.0780	-87.6096
	Muyil Cenote3	20.0779	-87.6098
	Laguna Muyil	20.0753	-87.6075

Appendix C. Well installation schematic and surficial geology of groundwater well sites in the Sian Ka'an Biosphere Reserve.

Well: SKP-1

Well: SKP-2

VITA

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PRESENTATIONS

Lagomasino, D., Campbell, P.K., and Price, R.M. 2010. Seasonal spectral dynamics and carbon fluxes at core EOS sites using EO-1 Hyperion images. American Geophysical Union. B411-0439. San Francisco, CA. December 2010.

Lagomasino, D., Campbell, P.K.E., and Price, R.M. 2011. Monitoring hydrogeochemical interactions in coastal mangroves in Everglades National Park using field spectroscopy and remote sensing. American Geophysical Union. San Francisco, CA. December 2011.

Lagomasino, D., Price, R.M., and Campbell, P.K.E. 2012. Seasonal water chemistry and spectral reflectance in coastal mangroves. 9th INTECOL International Wetlands Conference. Orlando, FL. June 2012

Lagomasino, D., Wlostowsk, A., and Mahmoudhi, M. 2012. Comparing hydrogeological drivers among LTER ecosystems and their effects on productivity, sedimentation, and social constructs. Long-Term Ecological Research All-Scientists Meeting. Estes Park, CO. September 2012.

Lagomasino, D., Price, R., Whitman, D. and Campbell, P. 2013. Hydrologic signals and patterns in coastal mangrove communities using space-borne remote sensing. AGU Meeting of the Americas. Cancun, MX. May 2013

Lagomasino, D., and Price, R. 2013. Tracing coastal and estuarine groundwater discharge sources in a complex faulted and fractured karst aquifer system. AGU Meeting of the Americas. Cancun, MX. May 2013

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PUBLICATIONS

Campbell, P.K.E., Middleton, E.M., Thome, K.J., Kokaly, R.F., Huemmrich, K.F., *Lagomasino, D.*, Novick, K.A., Brunsell, N.A. 2013. EO-1 Hyperion Reflectance Time Series at Calibration and Validation Sites: Stability and Sensitivity to Seasonal Dynamics. IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing. Vol.6, no.2, pp.276,290. April 2013. DOI: 10.1109/JSTARS.2013.2246139

Lagomasino, D., Corbett, D.R., and Walsh, J.P. 2013. Influence of wind-driven inundation and coastal geomorphology on sedimentation in two microtidal marshes, Pamlico River Estuary, NC. Estuaries and Coasts. DOI: 10.1007/s12237-013-9625-0

Lagomasino, D., Price, R., Whitman, D., Campbell, P., and Melesse, A. (under review at Remote Sensing of Environment). Estimating estuarine hydrogeochemistry using lead and satellite reflectance in two coastal mangrove communities.

Lagomasino, D., Price, R., Whitman, D., Campbell, P., Melesse, A., and Oberbauer, S. (submitted to Agricultural and Forest Meteorology). Spatial and temporal variability in spectral-based evapotranspiration measured from Landsat 5TM across two mangrove ecotones.

Lagomasino, D., and Price, R. (submitted to Limnology and Oceanography: Fluids and Environments). Connecting groundwater and surface water sources in a groundwater dependent coastal wetland: Sian Ka'an Biosphere Reserve, Quintana Roo, Mexico.