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COMPARISON OF KARSTIFICATION METHODS AND ISOSTATIC REBOUND IN THE SUWANNEE RIVER BASIN, FLORIDA

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Larche, Toni, "COMPARISON OF KARSTIFICATION METHODS AND ISOSTATIC REBOUND IN THE SUWANNEE RIVER BASIN, FLORIDA", Open Access Master's Thesis, Michigan Technological University, 2018.

<https://doi.org/10.37099/mtu.dc.etr/599>

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COMPARISON OF KARSTIFICATION METHODS AND ISOSTATIC REBOUND IN
THE SUWANNEE RIVER BASIN, FLORIDA

By

Toni L. Larche

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Geology

MICHIGAN TECHNOLOGICAL UNIVERSITY

2018

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE in Geology.

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Dedicated to my son, Tate Socko.

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Acknowledgements

Thank you, Dr. Jason Gulley for your support, guidance, and patience. Thank you to James, Chuck, and Charlie for all the encouragement and technical assistance.

Abstract

Plio-Pleistocene beach ridges in northern Florida are nearly 50 m above current sea level, but sea level during that time is not known to have been more than 25 m above current sea level. The height of beach ridges in northern Florida therefore create a conundrum because Florida is located on a passive margin in what is considered a tectonically stable environment. A series of recent studies have suggested that uplift on the Florida peninsula may be the result of the removal of subsurface crustal mass. Karstification of Florida's carbonate matrix may provide a mechanism for subsurface crustal mass removal and regional isostatic uplift. The ability of karstification to drive uplift was assessed using a calcium mass balance study of the Suwannee River Basin, in north Central Florida. Limestone dissolution in the entire basin was determined through statistical relationships between Ca^{2+} , which is the dominant cation in surface and groundwater and a primary component of calcite, and SpC and discharge. Because some water discharging from the Suwannee River Basin is also undersaturated with respect to calcite, maximum karstification potential for the basin was also calculated by assuming chemostatic conditions. Similar to past studies, isostatic uplift was calculated by assuming all dissolution occurred in the subsurface. Results from the application predicted anywhere from 77 to 6.7 mm k.y.⁻¹ of uplift, with three of the six methods between 24 to 29 mm k.y.⁻¹. Based on the results, karstification may be able to partially explain isostatic uplift of the northern Florida peninsula.

1. Introduction

Plio-Pleistocene beach terraces in Florida reach elevations of nearly 50 m above sea level (masl) (Pirkle and Czel, 1983). The origin of these beach ridges has remained problematic because sea level only reached 25 m during the Plio-Pleistocene, indicating that the beach ridges could not have formed 50 masl (Miller et al., 2005), and Florida's position on a passive margin means tectonic uplift of beaches that formed at lower elevations is unlikely. Previous work has consequently suggested that beach terraces in Florida could have possibly reached their present elevations via karstification of carbonate bedrock and isostatic uplift (Opdyke et al., 1984; Willet, 2006; Adams et al., 2010).

Isostatic rebound can be induced by any process that removes mass from the Earth's surface, because the crust "floats" on the mantle (Anderson and Anderson, 2010). Removal of crustal material causes the remaining crust to "float" higher in the asthenosphere. Isostatic rebound has typically been attributed to removal of crustal material by valley incision (Lucchitta, 1979), mountain erosion (Champagnac, 2007) or removal of ice through regional deglaciation (Farrand, 1962), (Figure 1). The dissolution of carbonate rock, otherwise known as karstification, also removes crustal mass, but much of the crustal mass is removed from the subsurface through processes of dissolution and cave formation.

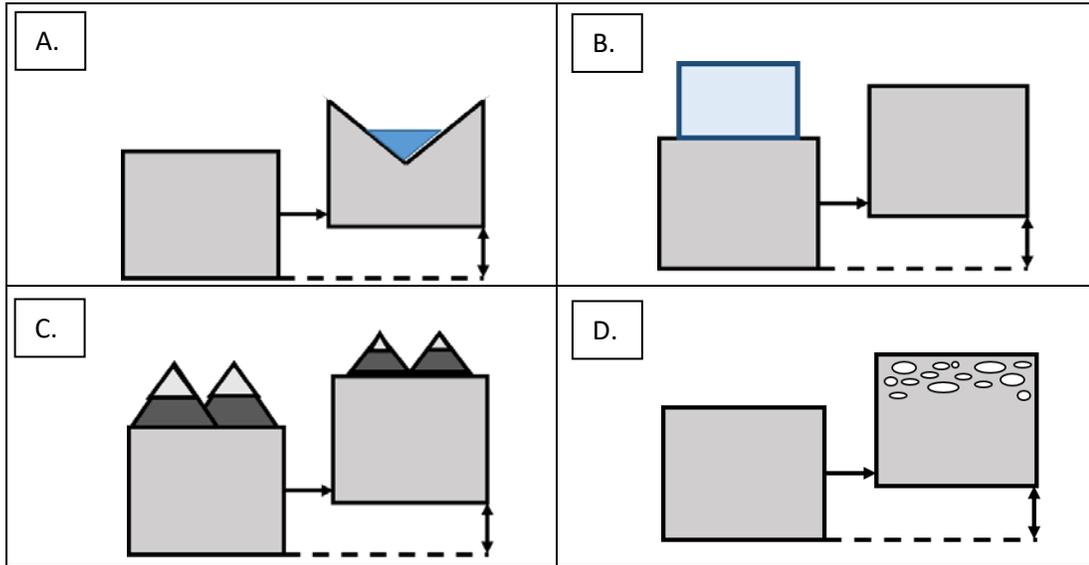


Figure 1: Methods of isostatic response by removal of crustal material. (A) Fluvial or glacial erosion incising the landscape and removing mass. (B) Regional deglaciation removes overlying mass from the crust. (C) Mountain erosion displacing sediment over a region (D) Karstification dissolves carbonate.

Isostatic rebound is not a one to one ratio between karstification and uplift, but instead accounts for several variables acting on the asthenosphere. Assuming surface denudation is negligible, the decrease in crustal density caused by karstification should allow for isostatic uplift, as described by the following equation:

$$U = \frac{\check{K}(\rho_{bi})}{\rho_{bi} + \rho_{eff}} \quad (1)$$

With U being uplift of the crustal plates, \check{K} yearly karstification of the crustal plate, ρ_{bi} representing original density of the carbonate matrix (2200 kg m^{-3}), and ρ_{eff} is the effective density of the thickness of the crustal plate, or the difference in mass between

the uplifted limestone matrix and that which remains below the original surface (200 kg m^{-3}) (Opdyke et al., 1984).

Three studies have investigated the role of karstification in driving uplift of the Florida Plateau, each arriving at different karstification and uplift rates (Table 1). Opdyke et al. (1984) calculated karstification based on the mass flux of total dissolved solids from springs (e.g. Rosenau and Faulker (1975), Rosenau et al. (1977), and Slack and Rosenau (1979)). Willet (2006) also relied on mass flux data from springs, but used a dataset with a larger number of springs over a larger area than the Opdyke study (e.g. Rosenau et al., 1977; Scott et al., 2002; and Scott et al., 2004). In both the Opdyke and Willet studies, modern karstification rates were assumed to be representative of karstification rates from the Plio-Pleistocene until the modern. Realizing that karstification rates were likely to vary due to climate variability between the Pliocene and the modern, Adams et al. (2010) created a numerical model that related karstification rates to rainfall:

$$\check{K} = \lambda \acute{P} \quad (2)$$

where \check{K} is the average karstification rate, \acute{P} is precipitation, and λ is a dimensionless parameter used as a calibration (tuning) factor. The tuning parameter was used to describe the efficiency of dissolution in the carbonate matrix needed for karst-driven changes in crustal density to uplift beach ridges to their current elevations before being removed by surficial erosion (Adams et al., 2010).

Table 1: Karstification and Uplift Rates of from previous studies: Opdyke et al. (1984), Willet (2006), and Adams et al. (2010).			
	Opdyke	Willet	Adams
Karstification (m k.y. ⁻¹)	0.0263	0.00733	0.0840
Uplift (m k.y. ⁻¹)	0.0241	0.00672	0.0770

Large differences in karstification and uplift rates calculated in these studies stem from differences in research methods. Studies of mass flux from individual springs relied on point measurements rather than time series data; consequently, the Opdyke et al., (1984) and Willet (2006) studies do not consider how temporal variability in spring discharge could impact carbonate relationships, and hence flux of dissolved solids from springs. Similarly, the Adams et al. (2010) model relates karstification to rainfall, but since the karstification model was not calibrated against observed karstification rates, its ability to represent actual karstification rates remains untested. Of particular concern is that the model relates karstification to rainfall rather than recharge. Evapotranspiration results in significant quantities of rainfall leaving the Florida carbonate platform as water vapor which does not transport dissolved solids.

In this study, several combinations of legacy data from the Suwannee River Basin were used to better constrain karstification and uplift rates in the Florida carbonate platform. Statistical relationships between daily average discharge and specific conductivity (SpC) measurements and measurements of Ca²⁺ concentrations in water samples collected at approximately monthly intervals at a United States Geological Survey gaging station near the mouth of the Suwannee River were used to estimate

karstification rates for the entire river basin. These results are compared to those of the Willet (2006), Opdyke et al. (1984), and Adams et al. (2010) studies.

2. Study Area

The Suwannee River basin is Florida's largest river basin. It is located in north-central Florida, extends into Georgia (Figure 2) and is approximately 28,000 km². The basin consists primarily of wetlands, forests, and farmlands (Ham and Hatzell, 1996). The Suwannee River Basin has subtropical climate (Crane, 1986). Average rainfall is ~132 cm y⁻¹ and evapotranspiration rates are between 90 and 105 cm y⁻¹, but large annual variations in both are common (Crane, 1986).

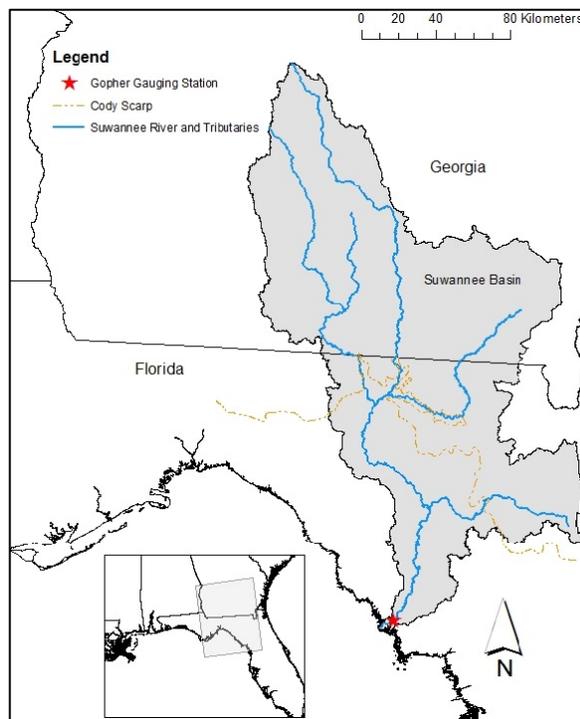


Figure 2: Map of the Suwannee River Basin, including the Gopher Gaging Station. Created using ArcMap.

In the upper 70% of the Suwannee River Basin, the Hawthorn group, Miocene in age, is exposed at the surface. The Hawthorn group is composed of fine to coarse sands,

silts, and clay materials. The Hawthorne group overlies the Ocala Limestone and acts a confining unit for the upper Floridian aquifer. In the lower 30% of the basin, the Hawthorn group has been removed by erosion and the Suwannee and Ocala limestones are exposed at the surface. Ocala is a fossiliferous limestone interbedded with dolostone and is Eocene in age, whereas the Suwannee Limestone a vuggy, muddy limestone that dates to the Oligocene (Scott et al., 1991; Martin and Gordon, 2000). The erosional limit of the Hawthorn Group is the Cody Escarpment, a topographic break approximately 30m in relief (Martin and Gordon, 2000).

Dense networks of surface streams are present above the Cody Scarp. Many of these streams sink into the subsurface where the flow off the Cody Scarp into the Suwannee or Ocala Limestones. Below the Cody Scarp, there are only two main rivers, the Suwannee and its tributary the Santa Fe. Prior to the two rivers converging, the Suwannee River at Branford gaging station has an average discharge rate of $351 \text{ m}^3 \text{ s}^{-1}$. Both rivers receive a substantial quantity of their inflow from 18 first magnitude springs, which have flow rates greater than 2831.6 L s^{-1} , and 87 second magnitude springs, with flow rates between 2831.6 L s^{-1} to 283 L s^{-1} (Hornsby and Ceryak 1998). These first and second magnitude springs bring groundwater and dissolved limestone, to the surface. All rain falling in the Suwannee River Basin that is not lost to evapotranspiration is discharged via the Suwannee River to the Gulf of Mexico. There are no known submarine springs that discharge water from the Suwannee River Basin. This study focusses on calcium concentration data collected between July 1999 to August 2008 and specific conductivity data collected from October 2005 to September 2007. These time

frames were selected based on the longest amount of continuous, approved data provided by the USGS.

3. Methods

3.1 Water Flux from the Suwannee River Basin

The Gopher River gaging station (USGS 02323592) is located ~12 km from the terminus of the Suwannee River. Consequently, all water exiting the basin is measured at this station. Daily average discharge data were obtained from the USGS waterwatch online database (waterwatch.usgs.gov)

Discharge in the Suwannee River at the Gopher River gaging station is tidally influenced. During droughts, very high tides and anomalous barometric events, such as hurricanes, can cause discharge values to be negative. Only two days in our period of record were associated with negative daily average discharge values and both were treated as zero values.

3.2 Ca²⁺ Flux from the Suwannee River Basin

Karstification was quantified karstification by calculating the mass flux of calcite from the basin using three complementary approaches. In each case, the mass flux of calcite was determined on the basis of empirically derived relationships between dissolved Ca²⁺ concentrations measured in water samples that are collected at monthly intervals and discharge or specific conductance. Similar to Opdyke et al. (1984) and Willet (2006), it was assumed that all dissolved Ca²⁺ is derived from calcite dissolution and 1 mol of Ca²⁺ in solution is equivalent to 1 mol of CaCO₃ being exported from the basin.

3.3 Ca²⁺ Flux from Concentration-Discharge Relationships

Between July 1999, and August 2008 water samples were collected at monthly intervals and analyzed for major ions. Discharge ranges from 3.5×10^6 to 7.7×10^7 m³ d⁻¹. Data are available from the Suwannee River Water Management District data portal (mysuwanneeriver.com). Because daily discharge values are available for the entire period of record used in this work, the primary method of calculating Ca²⁺ flux relied on statistical relationships between Ca²⁺ and daily average discharge on the day of water sample collection, which was best described with a power law (Figure 3). Using the Generalized Reduced Gradient in the Solver Analysis with Microsoft Excel, four outliers (representing less than 4% of the data) were removed, improving the coefficient of determination from 0.4086 to 0.5052. The power law relationship was used to calculate Ca²⁺ concentrations, ranging from 5.5×10^6 to 4.5×10^7 mol d⁻¹, of water flowing through the Gopher River gaging station from daily discharge measurements and calculated daily Ca²⁺ flux from the basin by multiplying daily Ca²⁺ concentrations by daily discharge totals. We assessed error by comparing the modeled Ca²⁺ concentrations to the measured concentrations on days where measured concentrations were available.

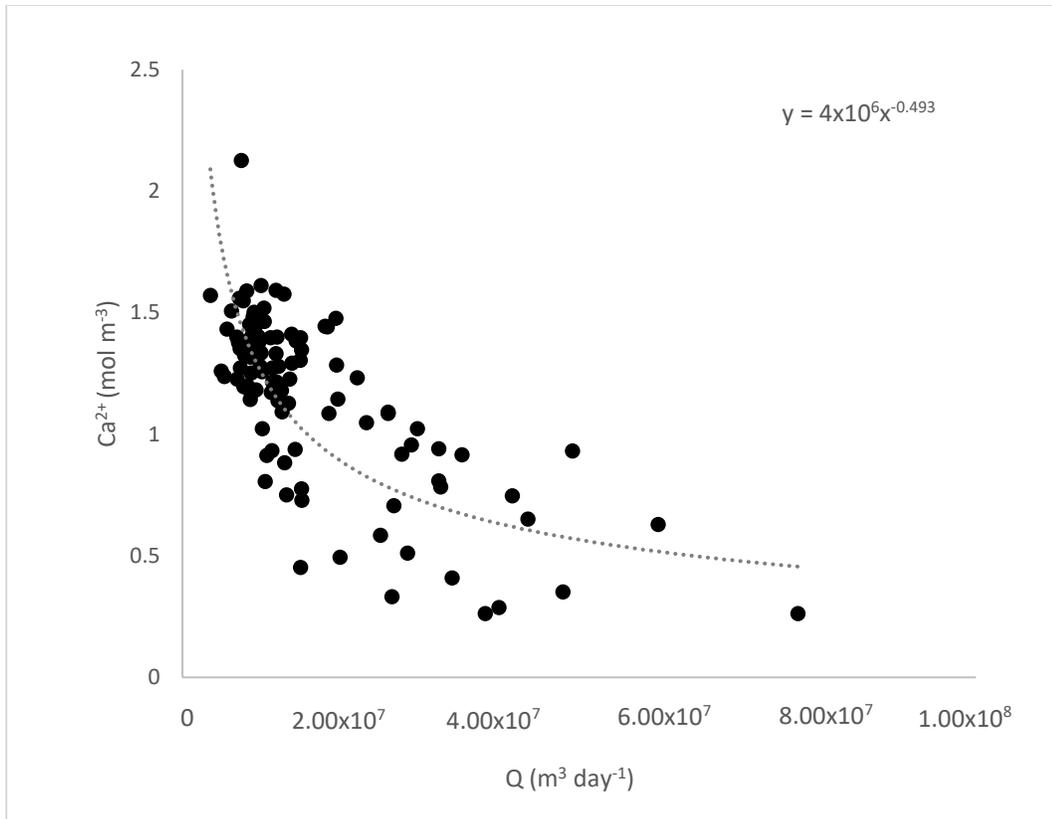


Figure 3: Ratings curve of Ca^{2+} compared to discharge (Q). Ca^{2+} decreases exponentially as a result of an increase in discharge at the Gopher River Station.

3.4 Ca^{2+} Flux from Concentration-Conductivity Relationships

The Gopher River gaging station continuously measured SpC and reported it as daily averages between 2005 to 2007 (data from USGS waterwatch online database). Because Ca^{2+} is the dominant cation in solution in limestone terrains, variation in SpC primarily reflects variation in Ca^{2+} concentration (Ford and Williams, 2007). The relationship between SpC and Ca^{2+} concentration in monthly water samples was fitted linearly (Figure 4). A least squares test resulted in the removal of two outliers (less than 6% of the data) improving the goodness of fit from 0.5375 to 0.9324. We used a linear relationship to calculate Ca^{2+} concentrations from daily average SpC and calculated daily

Ca^{2+} flux from the basin by multiplying daily Ca^{2+} concentrations by daily discharge totals. We assessed error by comparing the modeled Ca^{2+} concentrations to the measured concentrations on days where measured concentrations were available.

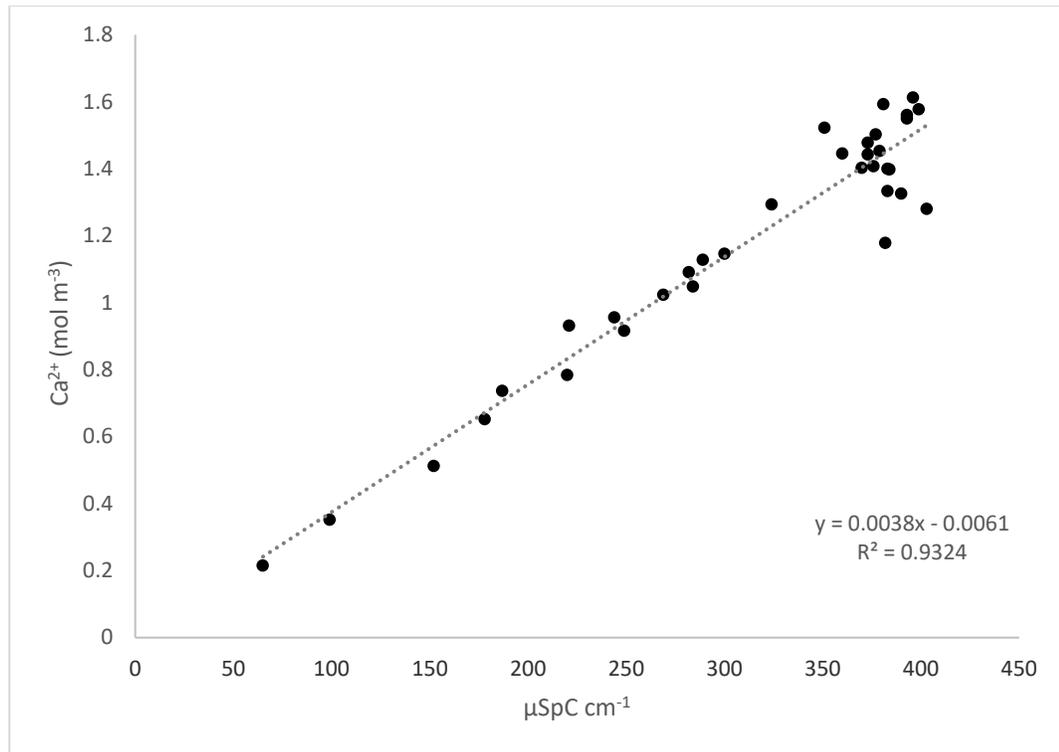


Figure 4: Ratings curve of specific conductivity (SpC) and Ca^{2+} . A positive linear relationship existed between SpC and Ca^{2+} with respect to discharge.

3.5 Chemostatic Ca^{2+} Flux

At low discharges, Ca^{2+} concentrations in the Suwannee River Basin remain constant with minor fluctuations in discharge (Gulley et al., 2013), indicating chemostatic conditions (Godsey et al., 2009). At higher discharges, Ca^{2+} concentrations decrease with discharge, indicating dilution. Because dilution indicates rainwater has not reacted to equilibrium with calcite bedrock, we decided to determine what the flux of Ca^{2+} would be

if dilution effects were removed and all effective rainfall reacted to equilibrium with calcite. By extending the chemostatic relationship between Ca^{2+} and Q at low discharges to the entire range of discharges, we were able to assess how much limestone would have likely been removed if all effective rainfall infiltrated the aquifer and participated in karstification. Ca^{2+} fluxes were therefore calculated by multiplying the average Ca^{2+} concentration at the terminus of the Suwannee River during chemostatic conditions, which we defined as any discharge lower than $300 \text{ m}^3 \text{ s}^{-1}$ (as determined in Gulley et al., 2013) by the total discharge. Physically, this approach would be the equivalent of removing the impermeable confining layer from the entire Suwannee River Basin. From a modeling standpoint, we consider the chemostatic scenario to represent the maximum amount of karstification that we would expect to occur in the Florida carbonate platform.

3.6 Karstification

Similar to the Opdyke and Willet studies, we calculate karstification assuming Ca^{2+} in solution was derived only from dissolution of the Ocala Limestone. We calculated the volume of calcite dissolved from the basin over each measurement interval by summing the total Ca^{2+} flux from the basin using the three methods described above. We converted the molar flux to volume of calcite dissolved by assuming a molar volume for calcite of $36.934 \text{ cm}^3 \text{ mol}^{-1}$ (Robie et al., 1984) and we assumed a porosity of 30% to calculate the volume of Ocala limestone dissolved (Budd and Vacher, 2004). We express karstification as the volume of Ocala limestone dissolved by normalizing it to the area of the Suwannee River Basin, calculated from ArcMap.

3.7 Uplift

Similar to the Opdyke and Adams studies, we calculated uplift resulting from karstification over a 1.6 million year time period using equation 1. Uplift rates were calculated based on karstification rates obtained using the Ca^{2+} -Q, SpC- Ca^{2+} and chemostatic relationships. We assumed that these karstification rates were representative of the last 1.6 million years, that all dissolution occurred in the subsurface and that surface denudation was insignificant in comparison to subsurface karstification. In actuality, karstification and uplift rates would be lower than modern during periods of lower sea levels and their associated drier climates.

3.8 Rainfall and Evapotranspiration

While rainfall data does not factor into our calculation of karstification, we assess relationships between rain falling on the Suwannee River Basin and the volume of water leaving the basin as discharge to determine how reasonable rainfall might be as a dissolution indicator. We assume the difference between rainfall and discharge is approximately equal to evapotranspiration over annual timescales (Kirchner, 2009). Because rainfall that evaporates or transpires to the atmosphere does not export Ca^{2+} from the basin, rainfall may not be an ideal proxy for dissolution.

Rainfall data was collected from 12 USGS rain gauge stations located inside and adjacent to the basin. A majority of the rain gauging stations had 4 to 14 years of available daily rainfall data, with 75% of the stations having a decade or more of data. The volume of rain falling in the basin was calculated using Thiessen Method via ArcGIS

10.2.2. Polygons were adjusted through time, so that the number of polygons increased

each time a new rain gage came on line. Precipitation was averaged over a two year period from 2005 to 2007. The period was selected based on having 10 operational rain stations, the most out of all the years, allowing for the greatest distribution of available data collection points over the basin.

4. Results

4.1 Rainfall and Evapotranspiration

Annual rainfall totals between 2001 and 2008 ranged from a high of 1.46 m y⁻¹ in 2004 to a low of 0.95 m y⁻¹ in 2007, with an average annual of 1.21 m (Figure 5).

Average annual discharge from the Suwannee River Basin, normalized to drainage basin area, ranged from 0.61m y⁻¹ in 2005 to 0.12 m y⁻¹ in 2002, resulting in an annual average discharge, and hence effective rainfall, of 0.26 m y⁻¹ from 2001 to 2008.

Evapotranspiration was determined to be 0.94 m y⁻¹ or 78% of the annual rainfall.

Maximum evaporation was 1.19 m yr⁻¹ in 2004 and was at a minimum in in 2005 with 0.64 m y⁻¹.

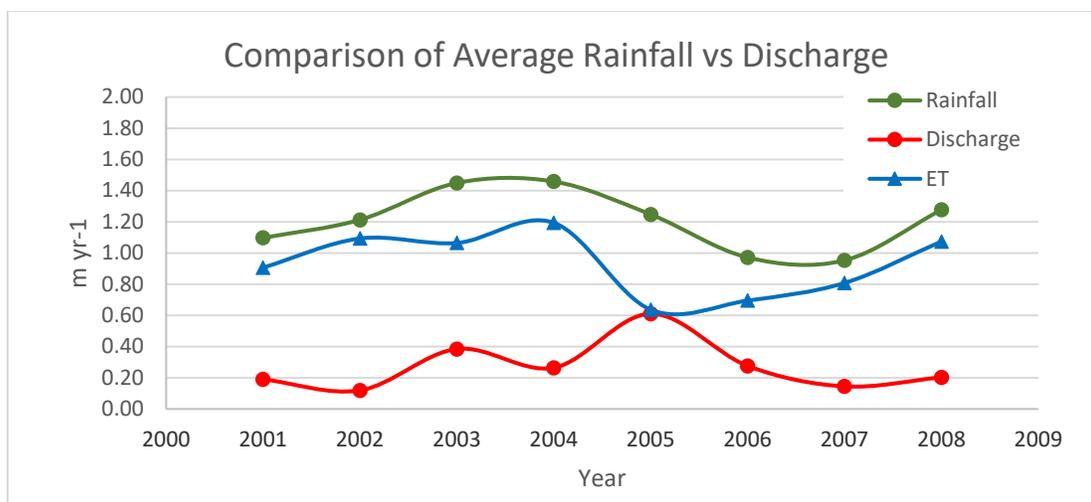


Figure 5: Comparison of annual rainfall, discharge at the Gopher River Station, and evapotranspiration over the Suwannee River Basin from 2001 to 2008.

4.2 Ca²⁺ Fluxes

Modeled daily fluxes of Ca²⁺ calculated from Ca²⁺-Q relationships varied from $\sim 3.14 \times 10^6$ to 4.27×10^7 mol d⁻¹ (Figure 6B). Modeled Ca²⁺ concentrations were similar to measured Ca²⁺ concentrations during at low flows estimated at 2×10^7 m³d⁻¹ (Figure 3) but varied with increased discharge. Over the entire period of record, average residual values were 0.92. Annual modeled Ca²⁺ flux varied from a low of 4.71×10^9 mol y⁻¹ in 2002 to a high of 8.74×10^9 mol y⁻¹ in 2005 and had a yearly average of 6.38×10^9 mol over the eight-year record (Table 2).

Table 2: Loss of Ca²⁺ from the Suwannee River as determined through Ca²⁺-Q, Chemostatic, and SpC-Ca²⁺ methods. The table reflects only years with full data available.

Year	Ca ²⁺ -Q	Chemostatic	SpC-Ca ²⁺
2000	5.37 x10 ⁹	5.65 x10 ⁹	
2001	5.33 x10 ⁹	5.98 x10 ⁹	
2002	4.71 x10 ⁹	4.45 x10 ⁹	
2003	8.40 x10 ⁹	1.44 x10 ¹⁰	
2004	7.61 x10 ⁹	1.30 x10 ¹⁰	
2005	8.74 x10 ⁹	1.59 x10 ¹⁰	
2006	5.85 x10 ⁹	7.52 x10 ⁹	6.29 x10 ⁹
2007	5.01 x10 ⁹	5.00 x10 ⁹	
Average	6.38 x10 ⁹	7.94 x10 ⁹	6.29 x10 ⁹

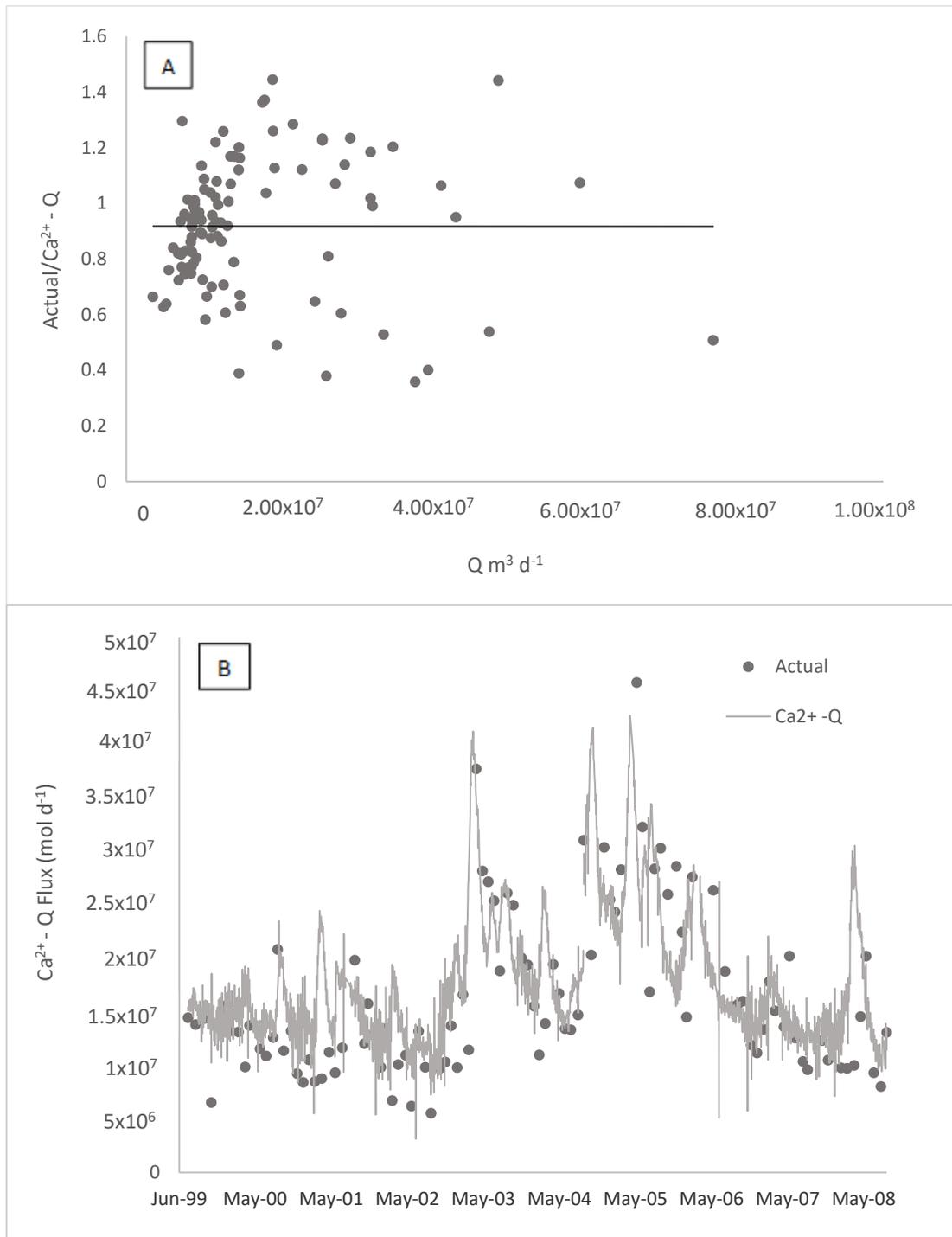


Figure 6: A) Residuals of actual flux measured at Gopher Station vs theoretical values calculated from the curve ratings. B) Time series of discharge with Ca²⁺ flux displayed as a line grey line while actual Ca²⁺ measurements are represented by black dots.

Modeled daily fluxes of Ca^{2+} calculated from SpC- Ca^{2+} ranged from 2.47×10^6 to $4.14 \times 10^7 \text{ mol d}^{-1}$ (Figure 7B). Residual errors varied little between baseflow and periods of increased discharge, resulting in an average residual value of 1.01 over the entire period of record (Figure 7A). Annual Ca^{2+} flux can only be modeled for 2006, the only year in our dataset with a complete SpC timeseries is $6.29 \times 10^9 \text{ mol y}^{-1}$.

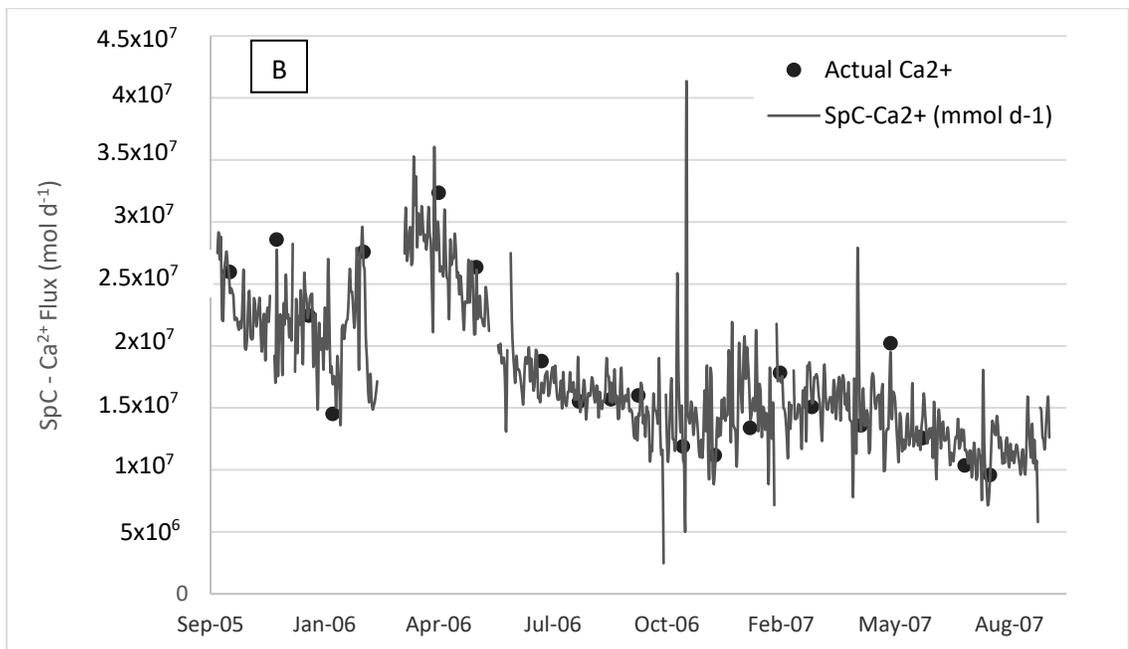
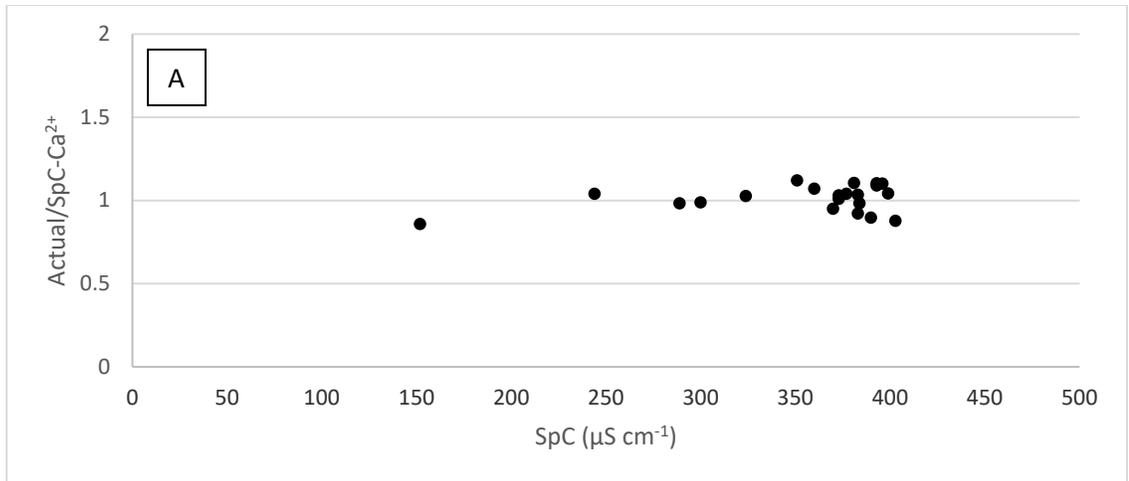


Figure 7: A) Residuals of actual flux measured at Gopher Station vs theoretical values calculated based on the linear relationship of Ca^{2+} to SpC. B) Time series of discharge with Ca^{2+} flux displayed as a line grey line while actual Ca^{2+} measurements are represented by black dots.

For the chemostatic model, fluxes of Ca^{2+} ranged from $\sim 7.19 \times 10^5$ to 1.23×10^8 mol d^{-1} (Figure 8). The lowest daily flux of 7.19×10^5 mol d^{-1} was in 2002, the driest year. The highest daily flux of 1.23×10^8 mol d^{-1} occurred in 2005, the year with the

highest rate of discharge from the basin. In 2005, the greatest annual loss of Ca^{2+} , 1.59×10^{10} mol was recorded during that nine-year period.

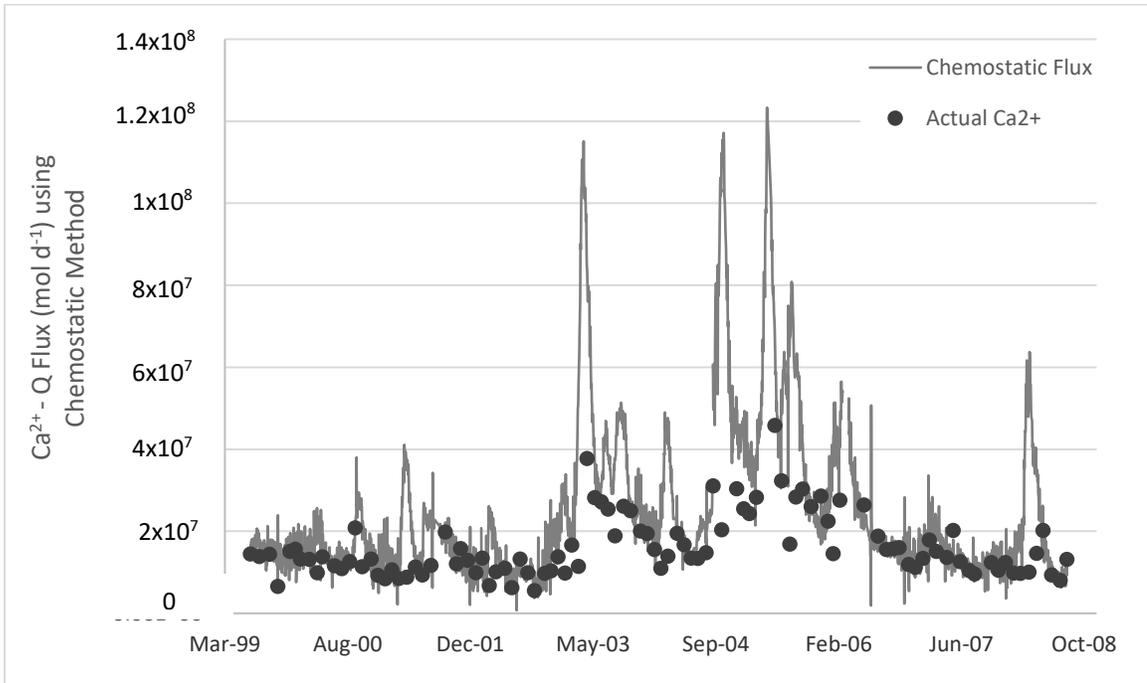


Figure 8. Time series of Ca^{2+} -Q Flux at Gopher River Station, from July 1999 to October 2008, applying the chemostatic method. The black dots represent actual flux measured from the station while the grey line represents the predicted Ca^{2+} flux using the chemostatic method.

4.3 Karstification

Average karstification rates were highest when we assumed chemostatic conditions and lowest when we used the SpC- Ca^{2+} model. Our karstification rates varied within 30% of one another: SpC- Ca^{2+} had the lowest rate at $35.50 \text{ k.y. m}^{-1}$, Ca^{2+} -Q at $34.48 \text{ k.y. m}^{-1}$ and the chemostatic method having the highest rate at $24.90 \text{ k.y. m}^{-1}$. In contrast, Opdyke et al. (1984) had slightly lower rates, at $41.45 \text{ k.y. m}^{-1}$, Willet's (2006) method was the slowest of them all, $148.83 \text{ k.y. m}^{-1}$ and Adams et al. (2010) had a

significantly higher rate of karstification when compared to the other methods at 12.99 k.y. m⁻¹ (Figure 9).

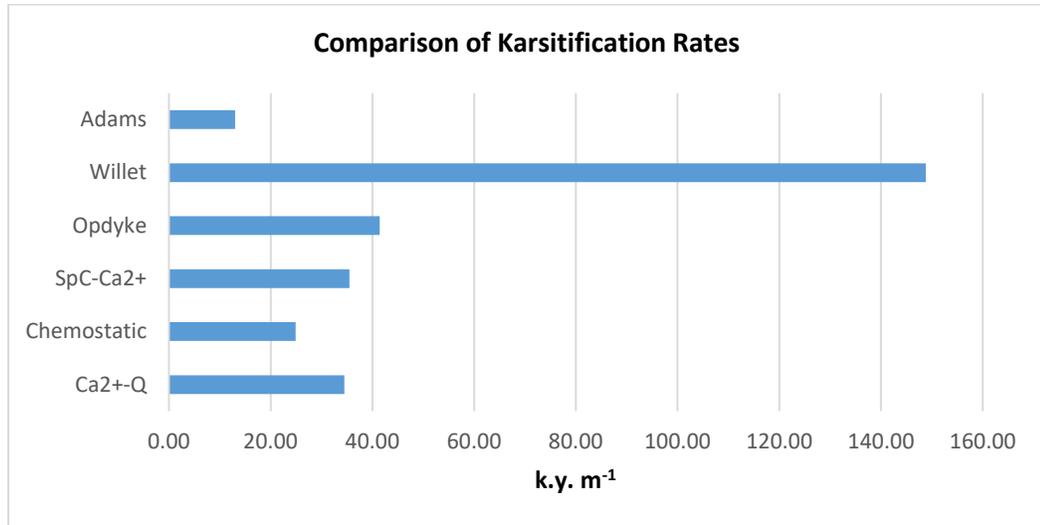


Figure 9: Comparison of karstification rates in thousands of years (k.y. m⁻¹) using all methods described in this study.

4.4 Uplift

Average annual uplift rates reflect annual karstification rates. Uplift rates were highest for chemostatic conditions and lowest for SpC-Ca²⁺. The uplift rates varied within 30% from the highest to the lowest rate: chemostatic with the highest rate at 40.2 m m.y.⁻¹, Ca²⁺-Q at 29.0 m m.y.⁻¹, and the SpC-Ca²⁺ method having the lowest uplift rate at 28.2 m m.y.⁻¹. Opdyke et al. (1984) and Willet (2006) had significantly lower average annual uplift rates at 24.1 m m.y.⁻¹ and 6.72 m m.y.⁻¹, respectively. Adams et al. (2010) uplift rate was higher than the other methods, resulting in 77.0 m m.y.⁻¹.

5. Discussion

Our three models of karstification and uplift are similar in magnitude to the estimates of Opdyke et al. (1984), but significantly greater than Willet (2006) and significantly lower than Adams et al. (2010). In the following section, we examine the limitations of our karstification model and suggest reasons for differences between our models and those of Opdyke, Willet and Adams.

5.1 Rainfall and Evapotranspiration

The primary driving force for karstification is effective rainfall (i.e. recharge) which infiltrates into carbonate bedrock subsurface. Our results suggest that, on average, 78% of annual rainfall is returned to the atmosphere via evapotranspiration. Because the Adams et al. (2010) model relates karstification to rainfall, rather than recharge, it may overestimate dissolution rates because water that leaves the basin through evapotranspiration does not export carbonate bedrock from the basin.

5.2 Comparison of Ca^{2+} -Q and SpC- Ca^{2+} Models

While the statistical relationships between Ca^{2+} -Q and SpC- Ca^{2+} were significantly different, the overall magnitude of karstification estimated by the two models differed by only 3%. The poor correlation between Ca^{2+} -Q is likely caused by hysteresis in the relationships between Ca^{2+} and Q (Gulley et al., 2011). Ca^{2+} concentrations in the Suwannee River basin are lower on the rising limb of the hydrograph, when rapid increases in river stage hydraulically dam inputs of Ca^{2+} rich groundwater from karst springs; Ca^{2+} concentrations are higher for equivalent discharges on the falling limb of flood hydrographs because Ca^{2+} -rich groundwater begins flowing

back into the river (Gulley et al., Dec 2013). Consequently, statistical relationships between Q and Ca^{2+} are weak. In contrast, SpC is a direct function of the number of ions in solution. Because Ca^{2+} is the dominate cation, statistical correlations between Ca^{2+} and SpC are strong and Ca^{2+} concentrations can be calculated from SpC records with reasonable accuracy during the rising and falling limb of individual flood events. The similarity in annual karstification rates calculated the SpC- Ca^{2+} and Ca^{2+} - Q models suggests that, while Ca^{2+} - Q relations do not describe instantaneous fluxes of Ca^{2+} particularly well, the residual errors cancel out and allow annual Ca^{2+} fluxes to be approximated with the same degree of accuracy as the SpC- Ca^{2+} model.

5.3 Chemostatic Model

Maximum theoretical karstification rates were calculated for the basin by assuming chemostatic conditions. Chemostatic conditions assume that all rainfall is able to infiltrate into the ground and equilibrate with carbonate minerals. While many of Florida's springs and spring fed rivers are essentially chemostatic, the Suwannee River Basin, like many of Florida's river basins, is not. Typically, the Suwannee River is chemostatic until discharge exceeds $300 \text{ m}^3 \text{ s}^{-1}$. Discharge that exceeds this threshold is derived from runoff from the upper 70% of the Suwannee River basin, which is overlain by low-permeability siliciclastics that generate runoff that has not reacted to equilibrium with carbonate minerals. During floods, the hydraulic head in the river becomes greater than the hydraulic head in surrounding groundwater, hydraulically damming groundwater inputs to the river and allowing the majority of floodwater to discharge to the Gulf of Mexico without reacting to equilibrium with carbonate minerals (Gulley et al., Dec

2013). Differences between our Ca^{2+} -Q and SpC- Ca^{2+} models with the chemostatic model suggest that if all runoff from the Suwannee River Basin were to react to equilibrium with calcite, average annual karstification rates would be 27-29% greater than predicted by our Ca^{2+} -Q and SpC- Ca^{2+} models. We thus consider the chemostatic model to be a theoretical maximum for karstification within the basin.

5.4 New Constraints on Karstification and Uplift

Our results provide new constraints on karstification and uplift rates for Florida. The Suwannee River Basin has well-documented hydrological boundaries, providing previously unavailable constraints on the footprint of karstification, and our statistical models allow Ca^{2+} flux to be estimated for the entire Suwannee River Basin at daily timescales. Willet (2006) and Opdyke et al. (1984) studies used coarse resolution sampling of karst springs, which do not account for temporal variability in carbonate fluxes and have only limited information to constrain drainage basin area. Groundwater flow patterns and unrecorded springs may alter the magnitude of Ca^{2+} removal from investigations not utilizing a delineated basin.

5.5 Comparison of Opdyke, Willet, and Adams Studies

Two of our long-term karstification models, Ca^{2+} -Q and SpC- Ca^{2+} , are similar in magnitude to Opdyke's et al. (1984) estimates. Since our models are within 3% of each other, we will compare the karstification rate of Ca^{2+} -Q, which had the slightly faster rate. Opdyke's et al. (1984) karstification rate was 17% lower than Ca^{2+} -Q. Willet's (2006) model used a similar approach but factored in a more robust dataset, which included a number of second and third magnitude springs collected in the early 2000s via

Scott et al. (2004), resulting in the use of over 400 springs for the study. Willet's (2006) had a karstification rate 77% lower than Ca^{2+} -Q and 72% lower than Opdyke's et al. (1984) calculation. Willet (2006) determined the difference for his lower rate was Opdyke et al. (1984) assumed higher values for carbonate lost through spring discharge. Willet (2006) argued he had a more robust dataset of spring discharge; however, the difference could be a result of flux per unit area. The study area Opdyke et al. (1984) used was the north central part of the Florida peninsula accounting for only 30% of the state. In contrast, Willet (2006) expanded his study area to cover as estimated 50% by including the Florida panhandle. When comparing the volume of water estimated to have discharged from the springs, Willet (2006) calculation of $2.29 \times 10^7 \text{m}^3 \text{d}^{-1}$ was only 18% greater than Opdyke's et al. (1984). Willet's (2006) expanded study area showed a decrease in flux per unit area when compared to Opdyke's et al. (1984), resulting in a decreased karstification rate of the carbonate matrix.

Our statistical models of karstification suggest that the numerical model used by Adams et al. (2010) significantly overestimate karstification. Karstification rates predicted by the Adams model are 62% greater than the Ca^{2+} -Q model and 48% greater than the chemostatic model. The inability of the chemostatic model to match the karstification rates of Adams et al. (2010) suggest that relating dissolution rates to rainfall, rather than recharge, would overestimate dissolution rates even if all effective rainfall was retained on, or within, the Florida carbonate platform until it equilibrated with carbonate bedrock.

5.6 Comparison of Uplift Calculations

While our results suggest that karstification can account for much of the uplift required to get the beach ridges to their present elevation, the models make a number of assumptions that may result in overestimation of uplift. Our models assume current climate conditions reflect past climate and do not account for known climate variability over the Plio-Pleistocene. We know that Florida had a much drier climate during glacial periods, suggesting that our karstification rates are too high. Decreased rainfall, particularly between 800 k.y. to 400 k.y., as suggested by Adams et al. (2010) from his model, would decrease the karstification rate, significantly so that the decrease in evapotranspiration rates would not be able to offset the loss of infiltrated water into the carbonate bedrock.

Because uplift rates are a direct function of karstification, discrepancies between uplift rates reflect discrepancies with karstification rates. Our Ca^{2+} -Q, SpC- Ca^{2+} , and chemostatic models produced uplift rates of 46.1 m, 45.1 m, and 54.4 m, respectively, within 1.6 m.y. Our uplift rates are therefore similar to, but slightly faster than Opdyke's et al. (1984) model which predicts 38.4 m of uplift during that same time period. In contrast, 6.82 m.y. are required for Willet's (2006) model to achieve 50 m of uplift but only 0.59 m.y. for Adams et al. (2010).

5.7 Unresolved Questions

Our models, along with Opdyke's et al. (1984) model, only provide 30-40 m of uplift of the 50m beach terraces. Additional mechanism would be needed in order to

account for the difference in height. One explanation was offered by Walcott (1972), describing farfield glacial isostatic adjustments along the east coast of the United States. Walcott (1972), suggests the removal of the Laurentide Ice Sheets of ice caused an isostatic rebound throughout much of the east coast, including Florida, which could account for the additional uplift needed. Indeed, the warped coastline indicates uplift is not driven by steady rate processes, but of varying karstification rates driven by precipitation and glacial isostatic rebound.

A second factor not accounted for was denudation of the surface over the period of study. Any mass lost over the surface would lower the resulting uplift. Willet (2006) and Opdyke et al. (1984) used an estimate of 10m of denudation. The extent to which the area experienced denudation is unknown.

6. Conclusion

The models presented in this study were used explain a significant portion of uplift observed in terraces in northern Florida. Previous models assumed calcium measurements taken from first and second magnitude springs across the region and did not account for yearly fluctuations in discharge. Other studies using precipitation as the driver for dissolution neglect evapotranspiration rates; therefore, not being able to predict fluxes of calcium into the oceans through discharge. Compared to previous work, our models encompass a defined study area based on the Suwannee River watershed, with discharge measurements taken from the pour point of a system.

The dissolution rates for our models were slightly faster than that determined by Opdyke's et al. (1984) model. However, since our models were derived under current

climate conditions, not necessarily reflecting that of intermittent glacial periods, we conclude that the Opdyke et al. (1984) model would be more suitable of that time period than the Adams et al. (2010).

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