Historical patterns of acidification and increasing CO_2 flux associated with Florida springs

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Introduction

Quantifying the contribution of springs and spring-fed rivers and streams to the west-central Florida carbon cycle is a critical step in improving our understanding of carbonate dynamics in these systems, refining CO_2 budget estimates, and identifying potential effects of discharge to the Gulf of Mexico. The goal of this research was to determine whether spring coast spring systems demonstrate significant changes in carbonate system parameters through time and space (Fig. 1). Assessing the chemical input of spring discharge on West Florida shelf waters was an additional goal of this study. Spring-vent hydrochemical parameters were compared to those measured at the stream-shelf interface for one spring group.

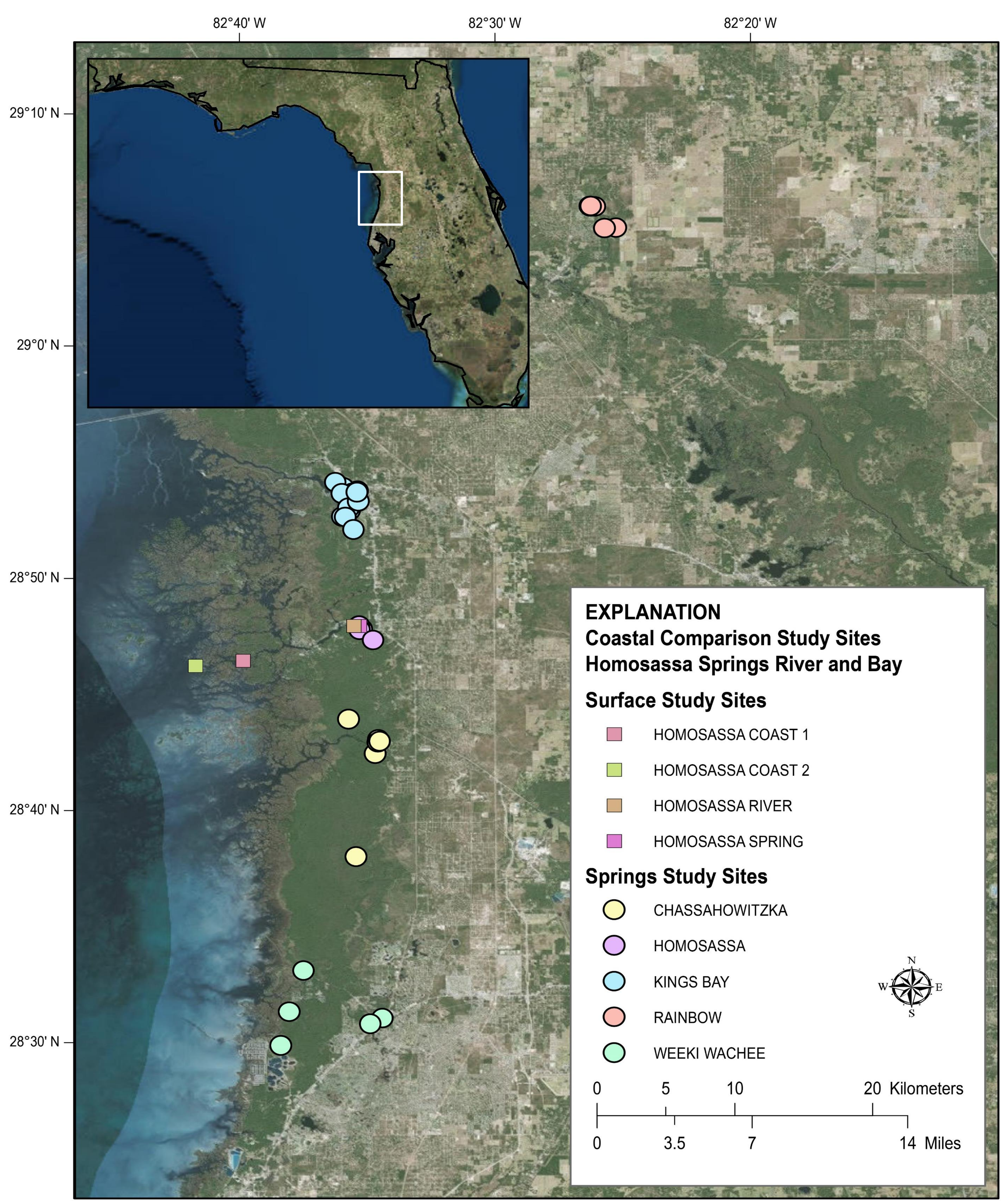

Figure 1. Study area, Florida Springs Coast, and locations of spring groups and study sites, including the locations of coastal comparison study sites for Homosassa Springs, River, and Bay

Methods

- Spring hydrochemical data (1991 to 2014) were obtained from the Water Management Information System (WMIS) database.
- Temperature, salinity, pH and TA data were aggregated seasonally.
- pCO_2 and air- water CO_2 flux calculated using CO2calc v.4.0.1 (Robbins et al. 2010), the dissociation constants of Millero (2010) and gas transfer velocity Raymond and Cole (2001).
- Statistical analysis conducted in Minitab v.17

Spring Group	Tot Sampling Events	Seasonally Aggreg. Sampling Events	pH	ALK uM/L	pCO_2 µatm	CO_2 flux mmol/m^2/d	Spring Surface Area m^2
WEEKI WACHEE	200	81					
Avg			7.31±0.01	2730.6±12.77	6067.28±208.94	1726.96±71.09	4889.85
CHASSAHOWITZKA	286	78					
Avg			7.31±0.01	3017.25±15.13	6773.16±189.21	1986.37±79.73	4973.93
HOMOSASSA	352	81					
Avg			7.44±.01	2255.57±11.11	4017.39±115.55	1111.81±40.40	9692.27
KINGS BAY	386	79					
Avg			7.59±0.01	2062.66±21.75	3174.26±126.72	878.79±44.88	27191.5
RAINBOW	397	77					
Avg			7.60±0.01	2031.05±22.34	4217.27±169.89	1267.05±74.53	2617.48

Table 1. Study spring groups data from 1991- 2014, mean carbonate parameter ± standard deviation, and spring surface area

Results

pH declined significantly throughout the study period. Decreases ranged from 0.15 in Homosassa Spring Group to as much as 0.36 in Weeki Wachee (Fig. 2). Based on 10-year forecasts, pH values will continue to decline through 2024 for all spring groups. Increases in TA varied from 90.9 to 347.6 µmol kg^{-1} and CO_2 flux rate increases from as low as 391.8 mmol m^{-2} day^{-1} to as high as 827.5 mmol m^{-2} day^{-1} were documented over time and across the five study spring groups (not shown). pCO_2 increased from 1,262.3 to 2,666.7 µatm, with linear regression, verifying significant increases (Fig. 3). The hydrochemistry of Homosassa Springs shows significant differences from the water of the Homosassa River and coastal sites (Fig. 4).

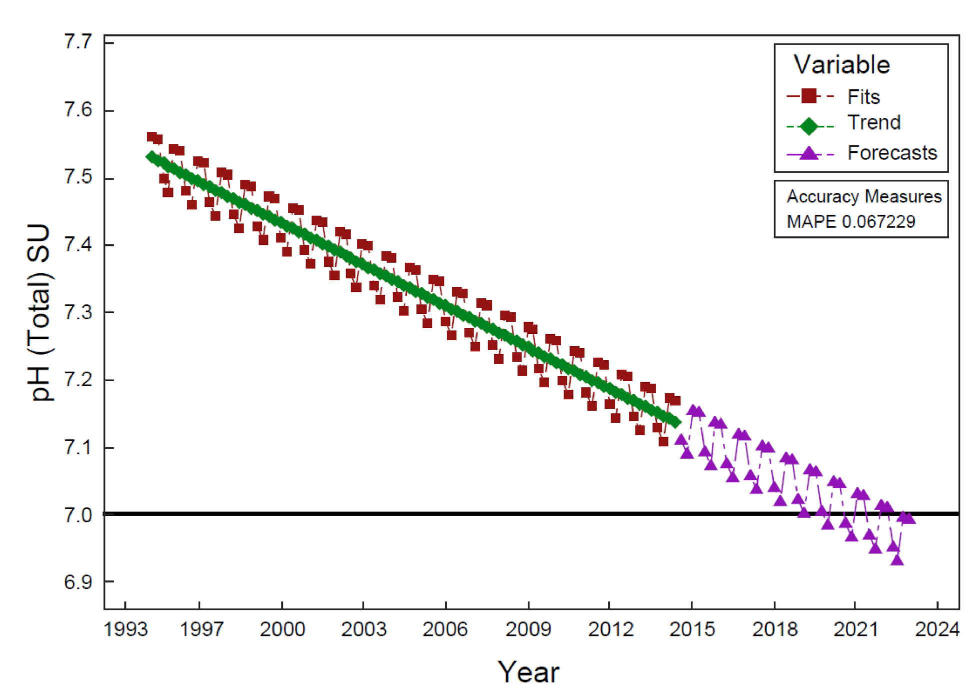

Figure 2. 10-year forecast for the Weeki Wachee Springs group pH based on observations from 1993 - 2014

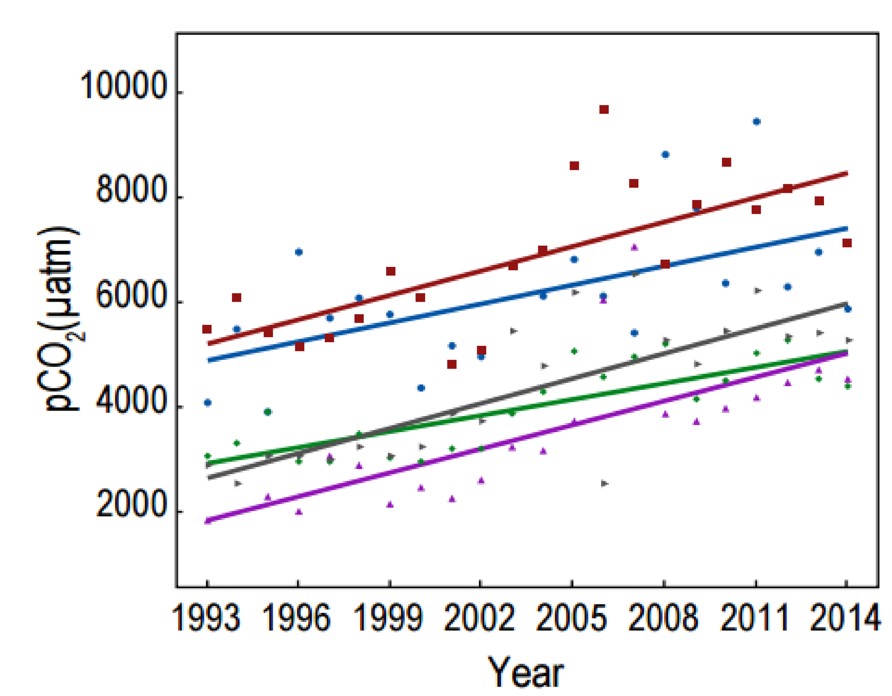

Figure 3. Linear regressions of spring group pCO_2 over study time period.

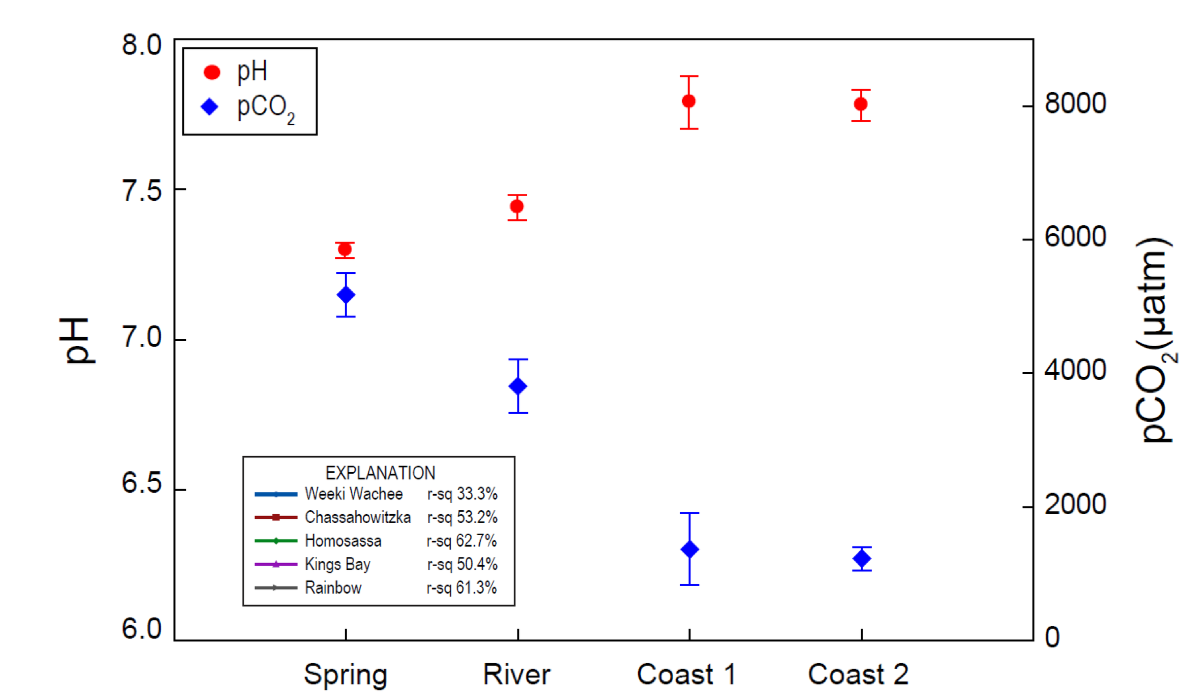

Figure 4. Interval plot of median pH and pCO_2 ± standard deviation for Homosassa Springs, River and coastal sites.

Conclusions

The five first-order- magnitude spring groups examined in this study were all supersaturated relative to atmospheric levels of CO_2 and, thus, sources of carbon to the atmosphere for the last two decades. All displayed statistically significant changes in carbonate parameters, including increases in acidity, alkalinity, and CO_2 flux over the time. Florida springs and spring-fed rivers demonstrate commonalities and similar trends as Florida riverine data and other aquatic systems, however unique their hydrogeology and hydrochemistry distinguishes them from expected norms. The results of this study have important implications for spring water quality, dissolution of the Florida carbonate platform, and identification of the effect and partitioning of carbon fluxes to and within coastal and marine ecosystems and highlights the importance of further research on carbon system parameters.

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