Historical patterns of acidification and increasing CO₂ flux associated with Florida springs

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Abstract

Florida has one of the highest concentrations of springs in the world, with many discharging into rivers and predominantly into eastern Gulf of Mexico coast, and they likely influence the hydrochemistry of these adjacent waters; however, temporal and spatial trends have not been well studied. We present over 20 yr of hydrochemical, seasonally sampled data to identify temporal and spatial trends of pH, alkalinity, partial pressure of carbon dioxide (pCO₂), and CO₂ flux from five first-order-magnitude (springs that discharge greater than 2.83 m³ s⁻¹) coastal spring groups fed by the Floridan Aquifer System that ultimately discharge into the Gulf of Mexico. All spring groups had pCO₂ levels (averages 3174.3–6773.2 µatm) that were much higher than atmospheric levels of CO₂ and demonstrated statistically significant temporal decreases in pH and increases in CO₂ flux, pCO₂, and alkalinity. Total carbon flux emissions increased from each of the spring groups by between 3.48 × 10⁷ and 2.856 × 10⁸ kg C yr⁻¹ over the time period. By 2013 the Springs Groups in total emitted more than 1.1739 × 10⁹ kg C yr⁻¹. Increases in alkalinity and pCO₂ varied from 90.9 to 347.6 µmol kg⁻¹ and 1262.3 to 2666.7 µatm, respectively. Coastal data show higher CO₂ evasion than the open Gulf of Mexico, which suggests spring water influences nearshore waters. 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.

The concentration of atmospheric CO₂ has increased substantially from pre-industrial levels of approximately 280 ppm to approximately 400 ppm today, and is predicted to continue rising (Royal Society 2005; Canadell et al. 2007; IPCC 2014; Keeling’s Curve at http://keelingcurve.ucsd.edu, accessed 04/04/2014). This increase represents only 25–50% of CO₂ emissions from anthropogenic sources because the ocean and terrestrial systems have sequestered the rest (Battin et al. 2009; Le Quéré et al. 2015). Total carbon dynamics within and between terrestrial, atmospheric, freshwater (surface and groundwater), and coastal and pelagic marine ecosystems are affected by increasing atmospheric CO₂ concentrations (Ver et al. 1999; Aumont et al. 2001; Richey 2004). Aquatic ecosystems such as rivers and streams laterally transfer carbon to the ocean and vertically to the atmosphere (Regnier et al. 2013). While the importance of lateral carbon fluxes from aquatic systems, especially rivers and streams, has been well documented (Sarmiento and Sundquist 1992; Wang and Cai 2004; Cole et al. 2007), carbon fluxes associated with spring systems have generally been overlooked (Mackenzie et al. 2005; Battin et al. 2008; McLeod et al. 2011). Quantifying carbon concentrations and associated fluxes in spring systems over time and space are critical components for defining the carbon cycle in ecosystems impacted by spring discharges and refining global carbon budget estimates (Archer 2005; Battin et al. 2009; Regnier et al. 2013). In Florida, springs play a major role in maintaining inland and coastal ecosystems. Springs from west-central Florida are fed by the Floridan Aquifer System (FAS) and subsequently discharge into the rivers, streams, and along the coast. In addition, springs are important features on the inner West Florida Shelf (WFS), where they are extensions of the coastal springs groups and likely significant sources of carbon; however, groundwater-related CO₂ evasion from carbonate platform spring systems remains virtually unstudied (Robbins et al. 2009).

Dissolved CO₂ in streams and rivers originates from a variety of sources, including respiration, allochthonous and autochthonous organic carbon oxidation, acidification of...
buffered waters, input of CO$_2$-rich groundwater, precipitation of carbonate minerals, and CO$_2$ respiration from the roots of vegetation (Butman and Raymond 2011). Regardless of the origin of CO$_2$, inland rivers and streams are predominantly supersaturated with CO$_2$ and are therefore a source of CO$_2$ to the atmosphere (Cole et al. 2007; Lohrenz et al. 2010; Butman and Raymond 2011; Lauerwald et al. 2013, 2015). Many Florida rivers and streams are spring fed, influenced by groundwater-surface water interactions. They contain waters reflecting their carbonate geology source, and therefore may not fit easily into existing predictive models for riverine CO$_2$ fluxes. Spring geochemistry and ecology are influenced by the discharge of chemically distinct groundwater with inorganic carbon and CO$_2$ degassing affecting pH. Further, biological activities, carbonate precipitation, and biochemical transformations are strongly influenced by the balance of spring water discharge geochemistry (Choi et al. 1998).

Determining the contribution of springs and spring-fed rivers and streams to the west-central Florida carbon budget is fundamental 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 the spring systems demonstrate significant changes in carbonate chemical parameters along temporal and spatial scales. This goal was accomplished by analyzing historical (1990s to 2014) pH, total alkalinity (TA), temperature, and meteorological data to calculate pCO$_2$ and CO$_2$ flux for five first-order-magnitude springs, whose discharge to the Gulf of Mexico. Hydrochemical parameters were compared geographically, and potential sources of variability such as land-use and hydrogeological factors within the springsheds are discussed. Assessing the chemical input of spring discharge on WFS waters was an additional goal of this study, accomplished by comparing spring-vent hydrochemical parameters to those measured at the stream-shelf interface for one spring group.

**Methods**

**Study area**

Florida’s Springs Coast is located on the west-central Gulf coast of Florida (Fig. 1), where more than 200 springs are found. This area is within the jurisdiction of the Southwest Florida Water Management District (http://www.sfwmd.state.fl.us/springs/springs-coast/ accessed March 2017). Five first-order-magnitude spring groups are located in the northern portion of the district, and each one discharges into rivers which subsequently discharge into the Gulf of Mexico; these groups were the focus of this study (Table 1; Fig. 1). Listed from south to north, with locations of the main springs, the spring groups are Weeki Wachee (latitude 28.5172, longitude -82.5732), Chassahowitzka (28.7154, -82.5762), Homosassa (28.7992, -82.5883), Kings Bay (28.8943, -82.5925), and Rainbow (29.1001, -82.4375) (Fig. 1; Table 1).

**Data collection and processing**

Spring hydrochemical data were collected and analyzed by SWFWMD and accessed from the Water Management Information System (WMIS) database (http://www.sfwmd.state.fl.us/ResData/Search/ExtDefault.aspx, accessed 2/5/2015). The dataset includes all springs selected for this study. Sampling was conducted by SWFWMD on an annual, biannual, or quarterly basis from 1991 to 2014. Spring vent water was sampled at low tide and analyzed in the field or at the Florida Department of Environmental Protection Bureau of Laboratories. Briefly, analytical procedures followed U.S. Environmental Protection Agency methods or standard methods in accordance with the Florida Administrative Code (Florida Department of Environmental Protection (FDEP) 2002). Hydrochemical parameters analyzed included temperature, salinity, calcium, nitrate-nitrite, pH$_{NBS}$, and TA along with the date and time of collection. Meteorological data (temperature and wind speed) from the Florida Automated Weather Network (FAWN) and atmospheric CO$_2$ measurements from the Mauna Loa Observatory were utilized for the calculation of pCO$_2$ and air-water CO$_2$ flux (http://www.esrl.noaa.gov/gmd/ccgg/trends/). Hydrochemical data from stations associated with each of the five spring groups (Tables 1, 2) were aggregated; data within each spring group were subsequently aggregated seasonally. Spring stations that were sampled at irregular intervals were excluded from the analyses. Missing spring water temperature values were estimated as the average of the three closest seasonal equivalents.

A comparison of carbonate chemistry parameters from the Homosassa Springs Group and its riverine and coastal surface water sites was conducted to characterize the effect of spring water discharge on the carbonate chemistry of coastal waters (Fig. 1). This was the only transect of a spring-to-coastal interface dataset in the database that contained temperature, salinity, pH, and TA (April 2008–February 2009) which are needed to calculate pCO$_2$ and CO$_2$ flux. The previously outlined methods for data preparation and processing were applied to these data, including their collation with meteorological and atmospheric CO$_2$ data.

**Calculation of pCO$_2$ and CO$_2$ flux**

The partial pressure of CO$_2$ was calculated using the inputs of TA and pH$_{Total}$ pairs (pH$_{NBS}$ was converted to pH$_{Total}$ using equations of Dickson 1984; Lewis and Wallace 1998), temperature, and salinity using the CO2calc program v.4.0.1 (Robbins et al. 2010), the dissociation constants of carbonic acid from Millero (2010) and HSO$_4^-$ from Dickson (1990), and total borate from Uppström (1974). Air-water CO$_2$ fluxes were also calculated using CO2calc using the gas transfer velocity constant of Raymond and Cole (2001), wind speed, atmospheric pCO$_2$, and water temperature. Specifically, CO$_2$ flux (i.e., the rate of CO$_2$ emissions from springs and surface water to the atmosphere) from each of the spring systems was calculated using the following equation:
Fig. 1. Study area within Florida’s Springs Coast, and locations of spring groups and study sites.
\[ \text{CO}_2 \text{ flux} \left( \text{mmol m}^{-2} \text{ day}^{-1} \right) = (\text{CO}_2w - \text{CO}_2a) \cdot K_0 \cdot k\text{CO}_2 \] \quad (1)

where \( \text{CO}_2w \) and \( \text{CO}_2a \) are the concentrations of \( \text{CO}_2 \) dissolved in the water and air, respectively, \( K_0 \) is the solubility of \( \text{CO}_2 \), and \( k\text{CO}_2 \) is the gas transfer velocity for \( \text{CO}_2 \) across the air–water interface. Total \( \text{CO}_2 \) evasion (\( \text{FCO}_2 \): mmol d\(^{-1}\)) was calculated for each spring group as follows:

\[ \text{FCO}_2 = A \cdot \text{CO}_2 \text{ flux} \] \quad (2)

where \( A \) is the spring group surface area (m\(^2\)) provided by Scott et al. (2004), and \( \text{CO}_2 \) flux was calculated from Eq. 1.

The units were then converted to kilograms or teragrams per year. A positive value indicates a \( \text{CO}_2 \) flux from the spring to the atmosphere, while a negative value indicates invasion of \( \text{CO}_2 \) into the spring.

### Statistical methods

The collection and processing methods described above resulted in the data utilized for all subsequent analysis (Barrera and Robbins 2017). Statistical analyses were performed using Minitab version 17 software (Minitab, State College Pennsylvania, U.S.A.). To describe decadal trends and longitudinal patterns of the water quality of spring groups, data

### Table 1. Locations and sampling event data from sampling stations associated with the five first magnitude spring groups.

| Spring group     | Station                      | Latitude  | Longitude | Sampling events | Total sampling events | Seasonally aggregated sampling events |
|------------------|------------------------------|-----------|-----------|-----------------|-----------------------|---------------------------------------|
| Weeki Wachee     | Jenkins Creek Spring         | 28.522    | -82.6341  | 59              | 200                   | 81                                    |
|                  | Weeki Wachee Main Spring     | 28.5172   | -82.5732  | 73              |                        |                                        |
|                  | Weeki Wachee Little Spring   | 28.5135   | -82.581   | 26              |                        |                                        |
|                  | Weeki Preserve Spring        | 28.4978   | -82.6396  | 25              |                        |                                        |
|                  | Wilderness Spring            | 28.5515   | -82.6245  | 17              |                        |                                        |
| Chassahowitzka   | Buford Spring                | 28.6335   | -82.5905  | 4               | 286                   | 78                                    |
|                  | Crab Creek Spring            | 28.7174   | -82.576   | 39              |                        |                                        |
|                  | Baird Spring                 | 28.7074   | -82.5781  | 46              |                        |                                        |
|                  | Chassahowitzka Main Spring   | 28.7154   | -82.5762  | 74              |                        |                                        |
|                  | Chassahowitzka #1 Spring     | 28.7162   | -82.5751  | 78              |                        |                                        |
|                  | Ruth Spring                  | 28.732    | -82.5955  | 45              |                        |                                        |
| Homosassa        | Homosassa #1 Spring          | 28.7992   | -82.5883  | 78              | 352                   | 81                                    |
|                  | Trotter Main Spring          | 28.7965   | -82.5864  | 80              |                        |                                        |
|                  | Homosassa #2 Spring          | 28.7992   | -82.5883  | 75              |                        |                                        |
|                  | Homosassa #3 Spring          | 28.7992   | -82.5883  | 75              |                        |                                        |
|                  | Pumphouse Spring             | 28.7964   | -82.5882  | 37              |                        |                                        |
|                  | Bluebird Spring              | 28.7886   | -82.5793  | 7               |                        |                                        |
| Kings Bay        | Black Spring                 | 28.8774   | -82.5992  | 26              | 386                   | 79                                    |
|                  | Tarpon Hole Spring           | 28.8818   | -82.5947  | 94              |                        |                                        |
|                  | Idiots Delight Spring        | 28.888    | -82.5894  | 31              |                        |                                        |
|                  | House Spring                 | 28.896    | -82.5897  | 8               |                        |                                        |
|                  | Catfish Spring               | 28.8982   | -82.5987  | 56              |                        |                                        |
|                  | Hunters Spring               | 28.8943   | -82.5925  | 68              |                        |                                        |
|                  | Millers Creek Spring         | 28.9019   | -82.604   | 16              |                        |                                        |
|                  | Magnolia Circle Spring       | 28.894    | -82.5997  | 25              |                        |                                        |
|                  | Parker Island Spring         | 28.8837   | -82.5953  | 25              |                        |                                        |
|                  | Three Sisters Spring #1      | 28.8883   | -82.5889  | 15              |                        |                                        |
|                  | Jurassic Spring              | 28.895    | -82.59    | 15              |                        |                                        |
|                  | Sid’s Spring                 | 28.8769   | -82.5975  | 4               |                        |                                        |
|                  | Golfview Boathouse Spring    | 28.8681   | -82.5919  | 4               |                        |                                        |
| Rainbow          | Rainbow Swamp #3 Spring      | 29.0847   | -82.4209  | 49              | 397                   | 77                                    |
|                  | Rainbow #6 Spring            | 29.0845   | -82.4284  | 73              |                        |                                        |
|                  | Bubbling Spring              | 29.1001   | -82.4348  | 74              |                        |                                        |
|                  | Rainbow #1 Spring            | 29.1001   | -82.4375  | 71              |                        |                                        |
|                  | Rainbow Bridge Seep North    | 29.1003   | -82.4378  | 58              |                        |                                        |
|                  | Rainbow #4 Spring            | 29.1002   | -82.4372  | 72              |                        |                                        |
were first tested for parametric distribution using Anderson–Darling test for normality. Non-normally distributed data were present in most of the datasets and guided the choice of subsequent statistical tests. Descriptive statistics for each parameter and springs group were calculated by year and season (Table 2). Descriptive statistics were calculated for Homosassa coastal site carbonate parameters and were compared to those from the Homosassa Springs Group dataset corresponding to the same study period (April 2008–February 2009) (Table 3).

To investigate the relationship between physical and carbonate chemistry parameters, Pearson correlation coefficients were calculated between nitrate-nitrite, dissolved calcium and pCO2, CO2 flux, TA, and pH. These associations were evaluated at a significance level of $\alpha = 0.05$ (Table 4). The Mann–Whitney test was used to examine the significance of the difference in parameters between the beginning (1991–1993) and the end of the study period (2012–2014). Time series and linear regressions of carbonate chemistry parameters were utilized to assess trends in pH, pCO2, and CO2 flux over time (Fig. 2a,b,c). Forecasts of trends using the additive model of decomposition, which accounts for trends and seasonality, were conducted for pH to predict changes in pH within the Weeki Wachee Springs Group. The accuracy measure for this analysis, mean absolute percentage error (MAPE), was found to be 0.9206 indicating that the model fit was excellent (Fig. 3). Mood’s median test was used to determine the significance of variations in mean carbonate parameters across all spring groups and in the Homosassa Springs Group spring-to-coastal interface dataset.

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**Table 2.** Study spring groups data from 1991 to 2014, mean carbonate chemistry parameters ± standard deviations, and spring surface areas. Spring surface areas were obtained from Scott et al. (2004) and do not include all sampling stations associated with the Springs Groups, as listed in Table 1.

| Spring group       | $pH_{Total}$ (SU) | Alkalinity (μmol kg$^{-1}$) | pCO2 (μatm) | CO2 flux (mmol m$^{-2}$ d$^{-1}$) | Spring surface area (m$^2$) |
|--------------------|-------------------|-------------------------------|-------------|-----------------------------------|---------------------------|
| **Weeki Wachee**   |                   |                               |             |                                   |                           |
| Avg                | 7.31 ± 0.01       | 2730.6 ± 12.8                 | 6067.3 ± 208.9 | 1727.0 ± 71.1                     | 4889.85                   |
| 1993–1995          | 7.57 ± 0.08       | 2717.7 ± 71.7                 | 4365.6 ± 966.7 | 1204.4 ± 437.5                    |                           |
| 2012–2014          | 7.21 ± 0.04       | 2814.4 ± 127.0                | 6814.4 ± 1335.0 | 1861.7 ± 180.9                    |                           |
| **Chasahowitzka**  |                   |                               |             |                                   |                           |
| Avg                | 7.31 ± 0.01       | 3017.3 ± 15.1                 | 6773.2 ± 189.2 | 1986.4 ± 79.7                     | 4973.93                   |
| 1993–1995          | 7.38 ± 0.05       | 2873.9 ± 36.9                 | 5592.8 ± 483.1 | 1541.7 ± 426.1                    |                           |
| 2012–2014          | 7.22 ± 0.07       | 3184.5 ± 54.4                 | 8131.6 ± 1259.7 | 2341.5 ± 389.1                    |                           |
| **Homosassa**      |                   |                               |             |                                   |                           |
| Avg                | 7.44 ± 0.01       | 2255.6 ± 11.1                 | 4017.4 ± 115.6 | 1111.8 ± 40.4                     | 9692.27                   |
| 1993–1995          | 7.51 ± 0.08       | 2205.4 ± 46.9                 | 3596.4 ± 928.6 | 974.3 ± 458.2                     |                           |
| 2012–2014          | 7.36 ± 0.07       | 2395.8 ± 49.5                 | 4858.8 ± 961.7 | 1366.1 ± 387.6                    |                           |
| **Kings Bay**      |                   |                               |             |                                   |                           |
| Avg                | 7.59 ± 0.02       | 2062.7 ± 21.8                 | 3174.3 ± 126.7 | 878.8 ± 44.9                      | 27191.50                  |
| 1991–1994          | 7.69 ± 0.18       | 2122.5 ± 274.7                | 2527.9 ± 1252.4 | 632.3 ± 471.8                    |                           |
| 2012–2014          | 7.45 ± 0.04       | 2203.3 ± 112.4                | 4592.0 ± 709.3 | 1286.0 ± 307.8                    |                           |
| **Rainbow**        |                   |                               |             |                                   |                           |
| Avg                | 7.60 ± 0.01       | 2031.1 ± 22.3                 | 4217.3 ± 169.9 | 1267.1 ± 74.5                     | 2617.48                   |
| 1993–1995          | 7.74 ± 0.09       | 1839.8 ± 108.9                | 2672.5 ± 689.1 | 748.4 ± 404.3                     |                           |
| 2012–2014          | 7.54 ± 0.03       | 2187.4 ± 35.0                 | 5339.2 ± 359.4 | 1575.9 ± 457.4                    |                           |

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**Table 3.** Mean carbonate chemistry parameters ± standard deviations for the Homosassa Springs Group, Homosassa River and coastal water sample sites.

| Sample site           | N   | $pH_{Total}$ (SU) | Alkalinity (μmol kg$^{-1}$) | pCO2 (μatm) | CO2 flux (mmol m$^{-2}$ d$^{-1}$) |
|-----------------------|-----|-------------------|-------------------------------|-------------|-----------------------------------|
| Homosassa Springs     | 5   | 7.30 ± 0.02       | 2312.7 ± 22.6                 | 4988.4 ± 325.6 | 1430.3 ± 99.6                     |
| Homosassa River       | 5   | 7.44 ± 0.04       | 2340.4 ± 10.6                 | 3591.0 ± 396.5 | 962.2 ± 40.6                      |
| Homosassa Coast 1     | 5   | 7.79 ± 0.09       | 2900.9 ± 31.4                 | 1814.6 ± 539.8 | 376.1 ± 78.9                      |
| Homosassa Coast 2     | 5   | 7.78 ± 0.05       | 2870.4 ± 47.2                 | 1192.8 ± 174.6 | 235.6 ± 61.0                      |
Table 4. Pearson correlation coefficient comparing of dissolved calcium and nitrate-nitrite with pH, alkalinity, pCO2, and CO2 flux at each springs group. *p < 0.05; **p < 0.01; p is not significant for values lacking asterisk.

|                      | Rainbow     | Kings Bay   | Homosassa    | Chassahowitzka | Weeki Wachee |
|----------------------|-------------|-------------|--------------|----------------|--------------|
|                      | Calcium     | Nitrate-nitrite | Calcium     | Nitrate-nitrite | Calcium     | Nitrate-nitrite | Calcium     | Nitrate-nitrite | Calcium     | Nitrate-nitrite |
| pH_total (SU)        | -0.527**    | -0.453**    | -0.478**     | -0.35**        | -0.311**    | -0.666**     | -0.715**    | -0.373**     | -0.557**    | 0.022         |
| Alkalinity (μmol kg⁻¹) | 0.864**    | 0.315**     | 0.589**     | 0.148          | -0.194      | 0.506**     | 0.288*      | 0.395**     | 0.086       | -0.174         |
| CO₂ (μatm)           | 0.145       | 0.434**     | 0.446**     | 0.159          | 0.096*      | 0.599**     | 0.387**     | 0.419**     | -0.033      | -0.099         |
| CO₂ flux (mmol m⁻² d⁻¹) | 0.17      | 0.422**    | 0.219       | 0.427**        | 0.093       | 0.447**     | 0.148       | 0.279*      | -0.089      | -0.039         |

Geographical analysis

Median pH and pCO₂ for 2014 were plotted north to south in SigmaPlot v. 12.0 (Systat Software, San Jose, California, U.S.A.) to assess the significance of spatial trends visually through interval plots (Figs. 4, 5). Additionally, mean carbonate parameters (pH, TA, pCO₂, and CO₂ flux) for spring groups and coastal water sites were imported as Excel spreadsheets and mapped in ArcGIS to geographically compare present-day variations in parameters. Shapefiles depicting springshed boundaries, land use, recharge, physiographic provinces, and potentiometric surfaces created by the SWFWMD (http://www.swfwmd.state.fl.us/data/gis/library/, accessed 12/5/2015) were clipped by springshed and used to qualitatively explore and assess variation in dominant land use, hydrology, and geomorphology among spring groups.

Results

The pH was the only parameter found to have declined throughout the study period (Table 2). The decreases ranged from 0.15 pH SU in the Homosassa Springs Group to as much as 0.36 in Weeki Wachee Springs Group. Increases in TA and pCO₂ varied from 90.9 to 347.6 μmol kg⁻¹ and 1262.3 to 2666.7 μatm, respectively, across study sites and over the study period. CO₂ flux rate increases from as low as 391.8 mmol m⁻² d⁻¹ to as high as 827.5 mmol m⁻² d⁻¹ were documented across the five study spring groups (Table 2). The Mann–Whitney test was used to examine the significance of changes in spring hydrochemistry over time. The results confirmed significant differences (p < 0.05) in pH, pCO₂, TA, and CO₂ flux for all of the spring groups except for Weeki Wachee CO₂ flux, which was not significant between the beginning and the end of the study period.

The pH, pCO₂, and CO₂ flux trends were explored further through linear regression. A significant decreasing linear trend and a seasonal pattern in mean pH values and significant increasing trends in pCO₂ and CO₂ flux (p < 0.01 for all parameters) were present in all spring groups over the study period (Table 5) (Fig. 2a,b,c). Based on 10-yr forecasts from these models, pH values are predicted to decline through 2024 for all spring groups. The most dramatic decrease is predicted at Weeki Wachee Springs Group, where trends project mean values to be as low as 6.95 by year 2024 (fitted trend equation: Yt = 7.5159 - 0.004749 × t) (Fig. 3).

Increases in nitrate-nitrite concentrations and dissolved calcium were highly correlated to pH decreases in all springs, except for nitrate-nitrite in Weeki Wachee Springs Group (Table 4). Mood’s median test of equality of medians revealed statistically significant differences in carbonate parameters, pH, TA, pCO₂, and CO₂ flux among spring groups (p < 0.01). Total carbon flux emissions per springs’ surface area were positive for each of the five study spring groups and were highest in Homosassa Springs Group at 2.13 × 10⁸ kg C yr⁻¹ and Kings Bay Springs Group at 5.62 × 10⁸ kg C yr⁻¹ at the end of the study period. In total, the springs currently emit more than 1.17 Tg C yr⁻¹.

Carbonate dynamics in Homosassa Springs Group and the coastal zone

The Homosassa Springs Group spring-to-coastal interface data set showed incremental increases in pH toward the coastal sites, with lowest values at the spring (7.30 ± 0.05), intermediate values at the river (7.44 ± 0.04), and higher values consistently at the coastal sites (7.78 ± 0.05) which were tidally influenced (Fig. 5). Mean carbonate parameters varied across the coastal surface water sites (Table 3). TA was also lowest in the springhead at 2312.7 μmol kg⁻¹, followed closely by the riverine sample site at 2340.4 μmol W⁻¹; the two coastal locations had mean TA values of 2900.9 and 2870.4 μmol kg⁻¹. Flux rate of CO₂ and pCO₂ values were highest in the spring sample site, decreasing from the river to the coastal sample sites.

Mood’s median test was used to determine the significance of pH, TA, pCO₂, and CO₂ flux variations within
Fig. 2. Linear regressions of spring group (a) pH, (b) pCO$_2$, and (c) CO$_2$ flux (from 1993 to 2014).
Homosassa Springs Group and the river and coastal surface water sites. All surface water site values for pH and CO₂ flux varied significantly \( (p < 0.01) \) from the Homosassa Springs Group median values for the same study period. There were also significant differences \( (p < 0.01) \) in pCO₂ and TA concentrations between Homosassa Springs Group and the two coastal surface water sample sites.

**Discussion**

Springs of West Central Florida are fed by the FAS therefore, this groundwater serves as the main regional source of spring CO₂, comparable to that measured in groundwater-fed lakes (Striegl and Michmerhuizen 1998; Champion and Starks 2001). Spring flow is generally through karst solution cavities in the confining FAS limestone and dolomite strata (Yobbi 1992) where it chemically interacts with the geologic formations. Studying the historical changes in the springs’ chemistry provides insight into long-term ecosystem as well as chemical changes in the aquifer. Although spring discharge hydrochemistry is a function of the water quality of the total flow system within a springshed (Copeland et al. 2011), numerous and diverse factors influence groundwater and consequently spring water quality, quantity, and chemistry (Upchurch 1992; Scott et al. 2004). These include climate, precipitation rates and chemistry, the geology/mineralogy and distribution of karst features, anthropogenic development of the area, pollution, groundwater withdrawals, the soil type in the recharge area, the residence time of the water in the aquifer, mixing of other waters in the aquifer system, and aquifer microbiology. Each of these factors influence the hydrochemistry of the groundwater; therefore, spring water is ultimately reflective of the evolving aquifer.

The decreasing trends in pH and increasing pCO₂ observed across all spring groups, coupled with increases in TA over the study period (1991–2014), generally agree with statewide trends for these parameters in lakes (Lazzarino et al. 2009) and springs (Copeland et al. 2011). The decline of pH values represent an increase in the acidity of study spring systems of 40–130% (with pH decreasing from 7.51 to 7.36 in Homosassa Springs Group, and from 7.57 to 7.21 in Weeki Wachee Springs Group, Table 2). The magnitude of...
this decline in pH is greater than that of the oceans, which are estimated to have increased in acidity by approximately 35% (with pH decreasing 0.1–0.2) since pre-industrial times because of increasing atmospheric pCO2 (Royal Society 2005; Doney et al. 2009). Over the 23 yr of this study’s dataset, atmospheric CO2 has risen from approximately 359 µatm to 401 µatm and has decreased the pH of Florida rainfall (Turk 1983; Nickerson and Madsen 2005; Bogan et al. 2009). However, this 40 µatm increase alone can only account for a 25% increase in acidity of rainfall to the springs’ recharge areas. The additional decreases in springs’ pH reflects the atmospheric contributions of sulfur dioxide and nitrous oxide. In general, Florida rainfall pH varies from <4.4 to 5.0 depending on a variety of factors, such as proximity to various anthropogenic sources of carbon dioxide, sulfur dioxide, and nitrous oxide (Hendry and Brezonik 1980; Prospero et al. 1987; Nickerson and Madsen 2005). Overall increases in springs’ acidity, however, result from hydrogeological influences, land use alterations, air emissions, human wastewater, animal waste, and fertilizer (Copeland 2011).

A reduction in pH and increasing TA in springs were also observed spatially, similar to observed trends in lake chemistry across Florida (Lazzarino et al. 2009). The two northernmost spring groups, Rainbow and Kings Bay, had the highest pH values and lowest TA values; and the southernmost study spring groups, Weeki Wachee and Chassahowitzka, exhibited the lowest pH values and highest TA. These patterns in spring chemistry likely reflect a variety of regional and local factors such as weathering of carbonate rocks (Striegl and Michmerhuizen 1998) along the southward trend of the aquifer, increase in the acidity of recharge water from acid rain and runoff, reduced residence time of recharge water due to increased groundwater withdrawals, and reduction in the ratio of diffuse relative to conduit flow. Further, decreases in aquifer recharge potential and rate coupled with land use changes, which vary by springshed, considerably influence spring discharge hydrochemistry (Martin and Dean 2001; Moore et al. 2009). Within Florida’s Springs Coast springsheds, groundwater withdrawals varied significantly during the study period (Ferguson 2015). In 2012, withdrawals ranged from 9 million gallons d⁻¹ (mgd) in the Homosassa Springs Group to 45 mgd in the Weeki Wachee Springs Group. Withdrawals of these magnitudes influence water potentiometry, discharge ratios, and groundwater contact.

Fig. 5. Interval plot of median pH and pCO₂ ± standard deviation for Homosassa Springs Group, Homosassa River and two coastal sites.

Table 5. Linear regressions of pH, pCO₂, and CO₂ flux for all Springs Groups (SP) in this study.

| Springs Groups     | pH          | pCO₂        | CO₂ flux     |
|--------------------|-------------|-------------|--------------|
| Weeki Wachee SG    | y = 43.27 - 0.01794 yr | y = -235908 + 120.8 yr | y = -47608 + 24.6 yr |
| Chassahowitzka SG  | y = 28.99 - 0.01082 yr | y = -337011 + 171.6 yr | y = -96551 + 49.18 yr |
| Homosassa SG       | y = 30.34 - 0.01143 yr | y = -238563 + 121.1 yr | y = -62026 + 31.51 yr |
| Kings Bay SG       | y = 39.38 - 0.01587 yr | y = -50859 + 128.3 yr | y = -89447 + 45.09 yr |
| Rainbow SG         | y = 28.88 - 0.01062 yr | y = -352083 + 177.9 yr | y = -95938 + 48.50 yr |
times with the aquifer surfaces, and reduces flow rates by 1–6% across spring groups. Additionally, land use changes associated with urbanization, including the conversion of forested areas in springsheds to agricultural and urban land uses, has affected drainage patterns through alterations in runoff and recharge rates which contributes to water quality impairment, including effects on water buffering capacity and inorganic carbon species (Katz 2004; Barnes and Raymond 2009; Aufdenkampe et al. 2011). In the southern spring groups, urbanization, increased transportation and extractive land uses have increased over the past 20 yr, and these land uses have a pronounced impact on water quality and chemistry (Brake et al. 2001; Raymond and Oh 2009). As a result of increased urbanization statewide, there was a 19-fold increase in nitrate concentration from the 1970s to 2000 (Scott et al. 2004). This trend is also observed in our dataset, where nitrogen is a predictor of pH decreases in all of the springs except Weeki Wachee Springs Group, the southernmost spring group, which showed some of the highest values of pCO2 and CO2 evasion. Weeki Wachee Springs Group nitrogen levels and rate of increase in this parameter were higher than that of Homosassa Springs Group, but less than Rainbow Springs Group. Based on the available data it is unclear why this parameter isn’t significant for this study site, but warrants further investigation. Decreasing pH of the water in the five springs is also highly correlated with increasing dissolved calcium, a strong indicator of increasing mobilization of calcium of the limestone platform.

Trends in pH values are predicted to continue to decline in all springs, and the Chassahowitzka and Weeki Wachee Springs Groups may be at or below pH 7 by the year 2024 (Fig. 3). This increasing acidity has implications for the dissolution rate of the coastal carbonate Floridan Platform. North to south trends in this region demonstrate a limestone loss rate of 1.3–17.83 cm yr⁻¹ (Willett 2005). Further declines in pH will increase dissolution and accelerate carbonate platform removal.

Spring groups in this study display mean pCO2 concentrations ranging well above that of the pCO2 of the atmosphere. Only a portion of the increasing pCO2 observed in historical data can be directly attributed to increasing atmospheric CO2 levels. The pCO2 values of the spring groups are within or above the range previously reported for regional and global riverine studies (2091–4902 μatm) (Jones et al. 2003; Aufdenkampe et al. 2011; Raymond et al. 2012; Lauerwald et al. 2013; Stackpoole et al. 2014; Lauerwald et al. 2015). The average CO2 daily flux rates for the spring groups in this study are all currently positive, ranging from 878.8 to 1986.4 mmol m⁻² d⁻¹ or 2.07 × 10⁴ kg m⁻² yr⁻¹ to 3.76 × 10⁴ kg m⁻² yr⁻¹, and the fluxes serve as a source of CO2 to the atmosphere. Further, latitudinal patterns were observed in both pCO2 and CO2 flux. The southernmost spring groups, Weeki Wachee and Chassahowitzka, which are associated with the most extractive or disturbed land use, demonstrated the highest pCO2 and CO2 flux values compared to northern spring groups, Homosassa, Kings Bay, and Rainbow Springs Groups, which are not associated with this type of development (Fig. 4).

The data reveal that over the past 20 yr, increasing CO2 emission to the atmosphere has occurred at all of the springs. Based on spring surface areas (Scott et al. 2004), total CO2 flux showed significant increases of annual carbon emission to the atmosphere from 1993 to 2013: 0.0348 × 10⁷ Tg C yr⁻¹ for Rainbow Springs Group, 0.286 × 10⁶ Tg C yr⁻¹ for Kings Bay, 0.0610 × 10⁷ Tg C yr⁻¹ for Homosassa, 0.0639 × 10⁷ Tg C yr⁻¹ for Chassahowitzka, and 0.0516 × 10⁷ Tg C yr⁻¹ for the Weeki Wachee Springs Group. The total yearly FCO2 for the end of the study period, 2013–2014, from the combination of the five spring groups in this study is 1.17 Tg C yr⁻¹. Vertical CO2 emissions for the springs are compared to other regional CO2 flux studies in aquatic systems in Table 6, however our estimates of carbon efflux are conservative and likely underestimate the contribution of CO2 flux from the springs because the surface areas

### Table 6. Comparison of total annual carbon emission (Tg C yr⁻¹) for rivers, lakes, estuaries, and springs.

| Aquatic system | Geographic location | Total carbon emission (Tg C yr⁻¹) | Citation |
|---------------|---------------------|----------------------------------|----------|
| Rivers        | Global              | 1800                             | Raymond et al. (2013) |
|               | Conterminous U.S.A. | 97                               | Butman and Raymond (2011) |
|               | Eastern U.S.A.      | 41.6                             | Stackpoole et al. (2014) |
|               | SE Coastal U.S.     | 6.4                              | Stackpoole et al. (2014) |
| Lakes         | Global              | 320                              | Raymond et al. (2013) |
|               | All                 | 114                              | Duarte and Prairie (2005) |
|               | All                 | 110                              | Cole et al. (2007) |
|               | Eastern U.S.A.      | 9.7                              | Stackpoole et al. (2014) |
|               | Florida             | 2                                | Lazzarino et al. (2009) |
| Estuaries     | Global              | 250                              | Cai (2011) |
|               | European            | 2                                | Frankignoule et al. (1998) |
| Springs       | 5 FL springs        | 1.17                             | This study |

Spring groups in this study display mean pCO2 concentrations ranging well above that of the pCO2 of the atmosphere. Only a portion of the increasing pCO2 observed in historical data can be directly attributed to increasing atmospheric CO2 levels. The pCO2 values of the spring groups are within or above the range previously reported for regional and global riverine studies (2091–4902 μatm) (Jones et al. 2003; Aufdenkampe et al. 2011; Raymond et al. 2012; Lauerwald et al. 2013; Stackpoole et al. 2014; Lauerwald et al. 2015). The average CO2 daily flux rates for the spring groups in this study are all currently positive, ranging from 878.8 to 1986.4 mmol m⁻² d⁻¹ or 2.07 × 10⁴ kg m⁻² yr⁻¹ to 3.76 × 10⁴ kg m⁻² yr⁻¹, and the fluxes serve as a source of CO2 to the atmosphere. Further, latitudinal patterns were observed in both pCO2 and CO2 flux. The southernmost spring groups, Weeki Wachee and Chassahowitzka, which are associated with the most extractive or disturbed land use, demonstrated the highest pCO2 and CO2 flux values compared to northern spring groups, Homosassa, Kings Bay, and Rainbow Springs Groups, which are not associated with this type of development (Fig. 4).

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used for calculations are only for those springs with surface vent areas listed in Scott et al. (2004). CO₂ evasion likely occurs over a larger area as the spring water mixes with stream water and travels to the ocean basin. Although Weeki Wachee and Chassahowitzka Springs Groups have the highest rates of efflux, they have the smallest surface areas; therefore, estimates likely will increase with more accurate surface area data. The pCO₂ and CO₂ flux increases are projected to persist based on the influence of decreasing trends in pH, increases in TA, and increases in atmospheric CO₂ concentrations.

Dissolved CO₂ in surface water and groundwater can originate from multiple sources, including biological sources such as dissolved soil CO₂, root respiration, and microbial respiration, oxidation of organic carbon, acidification of buffered water, acid rainfall, and geochemical processes associated with the dissolution and precipitation of carbonate minerals. Variability in CO₂ concentrations and fluxes from Springs Coast springs can be attributed to variation in the individual systems themselves, including surface areas of the springs, geology and physiography, climate, land use changes, hydrochemical concentrations, discharge, and hydrology within the springshed (Scott et al. 2004; Copeland et al. 2011). For example, land cover and use are different in each of the springsheds and likely influence the trends observed in the data. The specific processes that can be attributed locally to the variability of CO₂ in these individual springsheds are not addressed in this study but warrant additional investigation. Further, it is not known how the carbon fluxes of these coastal springs relate to groundwater seeps that are offshore and fed by the FAS. However, enriched radon-222 reflecting submarine groundwater discharge associated with the FAS was observed in the vicinity of several nearshore seep locations (Smith and Robbins 2012) where relatively high pCO₂ values for the WFS were recorded.

The acidification of coastal systems and estuaries can be buffered or accelerated by changes to riverine chemistry and discharge (Aufdenkampe et al. 2011), and these research results suggest this process likely occurs for springs as well. For example, the geochemistry of Homosassa Springs Group shows distinct, significant differences from the water of the Homosassa River and the Homosassa Bay coastal sites (Fig. 5; Table 3), with a transition from a groundwater-dominated spring system to a tidal driven riverine surface water to an estuarine coastal environment. The mean spring pH is 0.14 pH units lower than that of the closest riverine sample site and 0.48 pH units lower than those of nearby coastal surface water sites, which are marine and tidally influenced. Presently, TA values are lower in the spring vs. the riverine and coastal sample sites. However, predicted trends indicate a continued increase of springs’ TA, possibly as a result of the FAS hydrochemistry role in dissolution of the carbonate platform. Downstream changes in parameters reflect the influence of in-stream processes, including gas exchange from stream flow hydraulics and biological activity (e.g., photosynthesis, respiration, decomposition) (De Montety et al. 2011; Stackpoole et al. 2014). The mean pCO₂ values, 1192.8 μatm and 1814.6 μatm, for the Homosassa Springs Group coastal sample sites reflect a tidal influenced system and are comparable to the range of measurements for estuaries (400–10,000 μatm) (Cai 2011) and are lower than the river and spring sites. Although significant systematic differences between the hydrochemistry at the springs, river, and coastal sample sites are identified, more data are needed to quantify the effects of changes in the Homosassa Springs Group carbonate chemistry have on the river and coastal systems. Similar to studies that have documented declines in pH and increases in TA in rivers, estuaries, and coastal zones (Feely et al. 2010; Duarte et al. 2013; Kaushal et al. 2013), this study documents declining pH, increasing CO₂ flux, and increased TA trends are also occurring in Florida’s Springs Coast springs and rivers, which are transition zones to the coast. High CO₂ and low pH waters of FAS-fed springs provide important insight into geochemistry of water discharged into nearshore coastal waters.

**Conclusion**

The five first-order-magnitude spring groups examined in this study were all supersaturated relative to atmospheric levels of CO₂ and, thus, sources of carbon to the atmosphere for the last two decades. Florida springs and spring-fed rivers demonstrate commonalities between other Florida riverine data; however, unique hydrogeology and hydrochemistry must be considered because these factors distinguish them from riverine norms. Florida springs’ data trends demonstrate acidification and increases in alkalinity, pCO₂, and CO₂ flux, similar to trends occurring in other aquatic systems. This study highlights the importance of further research on carbon system parameters such as pH, TA, pCO₂, and CO₂ fluxes in spring’s systems that are influenced by the chemically evolving FAS water. More studies on the impact of these hydrochemically evolving springs discharging into and influencing coastal ecosystems are critical. Further study of this evolution is necessary to determine the ecological effects within these systems and influences of carbon on coastal interfaces of the Gulf of Mexico.

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Conflict of Interest

None declared.

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