Climate control of decadal-scale increases in apparent ages of eogenetic karst spring water

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Abstract

Water quantity and quality in karst aquifers may depend on decadal-scale variations in recharge or withdrawal, which we hypothesize could be assessed through time-series measurements of apparent ages of spring water. We tested this hypothesis with analyses of various age tracers ($^3\text{H}/^3\text{He}$, SF_6 , CFC-11, CFC-12, CFC-113) and selected solute concentrations [dissolved oxygen (DO), NO_3 , Mg, and SO_4] from 6 springs in a single spring complex (Ichetucknee springs) in northern Florida over a 16-yr period. These springs fall into two groups that reflect shallow short (Group 1) and deep long (Group 2) flow paths. Some tracer concentrations are altered, with CFC-12 and CFC-113 concentrations yielding the most robust apparent ages. These tracers show a 10 to 20-year monotonic increase in apparent age from 1997 to 2013, including the flood recession that followed Tropical Storm Debby in mid-2012. This increase in age indicates most water discharged during the study period recharged the aquifer within a few years of 1973 for Group 2 springs and 1980 for Group 1 springs. Inverse

correlations between apparent age and DO and NO₃ concentrations reflect reduced redox state in older water. Positive correlations between apparent age and Mg and SO₄ concentrations reflect increased water-rock reactions. Concentrated recharge in the decade around 1975 resulted from nearly 2 m of rain in excess of the monthly average that fell between 1960 and 2014, followed by a nearly 4 m deficit to 2014. This excess rain coincided with two major El Niño events during the maximum cool phase in the Atlantic Multidecadal Oscillation. Although regional water withdrawal increased nearly 5 fold between 1980 and 2005, withdrawals represent only 2 to 5% of Ichetucknee River flow and are less important than decadal-long variations in precipitation. These results suggest that groundwater management should consider climate cycles as predictive tools for future water resources.

Keywords: Groundwater Recharge, Groundwater Remediation, Florida Karst, Springs, Water Age, Atlantic Multidecadal Oscillation

1 Introduction

The time between recharge and discharge of groundwater (i.e., its residence time in the subsurface or “age”) is important for assessing the sustainability of groundwater, potential for aquifer contamination, and dissolution of soluble aquifer materials. Residence time is particularly critical in karst aquifers since they provide potable water to approximately a quarter of the world’s population (Ford and Williams, 2007). Karst aquifers have elevated and variable hydraulic conductivity, which can range between 10^{-5} to 10^{-1} cm/sec as dissolution and reprecipitation of soluble aquifer minerals alter permeability (Ford and Williams, 2007; Worthington et al., 2000). Elevated hydraulic conductivity allows rapid recharge of undersaturated water, particularly at point recharge sites such as sinkholes, enhancing dissolution (Brown et al., 2014; Gulley et al., 2011) and introducing surface contaminants (Katz et al., 2001), including waste waters (Mahler and Massei, 2007; Schmidt et al., 2013) and nutrients (Boyer and Pasquarell, 1995; Molenat et al., 2008; Pretty et al., 2006). The large range in hydraulic conductivity causes variable residence times for groundwater that may allow rapid contaminant transport through the aquifer or alternatively increase time available for contaminant remediation, and thereby alter the impact of contaminants to ecosystems in receiving streams and coastal waters (Cohen et al., 2012; Lapointe and Matzie, 1996). For most karst aquifers, the distribution of hydraulic conductivity is unknown, so numerical models of specific aquifers rely on randomized permeability distributions, which may limit their usefulness in addressing specific management question (Butscher and Huggenberger, 2008; Hartmann et al., 2013). Therefore, characteristic residence times are critical to management of karst aquifers but difficult to identify through modeling. Residence times have been determined in karst aquifers (for some examples see Katz, 2004; Katz et al., 2001; Long and Putnam, 2006; Long and

Putnam, 2009; Plummer et al., 1998a; Plummer et al., 1998b) although never at a single location over long time periods. Such analyses could be used to evaluate how residence times change with varying environmental and recharge conditions (as described in for example, Martin and Dean, 2001; Ryan and Meiman, 1996; Shuster and White, 1972), a hypothesis we test here.

Residence time of groundwater has been estimated using various chemical and isotopic tracers with known time-varying inputs that are derived from the atmosphere or aquifer materials (Bethke and Johnson, 2008; Busenberg and Plummer, 1992; Busenberg and Plummer, 2000; Darling et al., 2012; Delbart et al., 2014; Groning et al., 2006). The best tracers are characterized by concentrations that change at time scales similar to characteristic residence times, which can range from hours to decades, depending on permeability structures of the aquifers. Tracers useful at these time scales include chlorofluorocarbons (CFCs), ^3H , ^3He , and SF_6 (Busenberg and Plummer, 1992; Busenberg and Plummer, 2000; Cook and Solomon, 1997; Plummer et al., 1998a; Plummer et al., 1998b). Most tracers do not represent a single residence time, but instead an average distribution of residence times for multiple water parcels with distinct flow paths (Bethke and Johnson, 2008; Małoszewski and Zuber, 1982; Suckow, 2014; Varni and Carrera, 1998). Consequently, tracer-based residence times are commonly referred to as “apparent ages” (Jurgens et al., 2012; McCallum et al., 2012). Tracer-derived apparent ages may be altered through tracer reactions with aquifer material, and by diffusive interactions between zones of differing permeability within the aquifer. Many causes of alterations are known and may be evaluated using multiple tracers for single water samples (Turnadge and Smerdon, 2014). With appropriate corrections for alteration, useful information may be gleaned about long-term recharge characteristics (Darling et al., 2012; Suckow, 2014).

Karst aquifers fall into a spectrum between two end-members: those that have lost primary porosity during burial diagenesis (telogenetic karst) and those that retain their primary porosity (eogenetic karst, Vacher and Mylroie, 2002). These end-members would be expected to have differing residence time distributions (e.g., Florea and Vacher, 2006; Florea and Vacher, 2007; Martin and Dean, 2001; Shuster and White, 1972). Available storage in telogenetic karst is mostly in conduits and fractures (Worthington et al., 2000) and may have short residence times, especially following large recharge events (e.g., Meiman et al., 1988; Shuster and White, 1972). In contrast, most eogenetic karst storage is in primary porosity of the matrix rocks and should have longer residence times than telogenetic karst (Florea and Vacher, 2006; Florea and Vacher, 2007; Martin and Dean, 2001). Some flow occurs through the matrix porosity although some flow also occurs through conduits, which could decrease apparent ages following large recharge events (Iqbal and Krothe, 1995; Iqbal and Krothe, 1996; Shuster and White, 1972).

To test these hypotheses, we analyzed apparent ages of water discharging from the upper Floridan aquifer at six springs within the Ichetucknee springs group in north-central Florida (Fig. 1). Apparent ages were evaluated with CFC-11, CFC-12, CFC-113, and SF₆ concentrations and ³H/³He ratios for samples we collected between 2009 and 2013, mostly in the year following Tropical Storm Debby, which passed through the region in June 2012. We compare these new apparent ages with apparent ages reported previously for water collected between 1997 and 2003 (Happell et al., 2006; Katz, 2004; Katz et al., 2001; Katz et al., 2004; Katz et al., 1999). We aim to evaluate how eogenetic karst aquifers may respond to both short term individual precipitation events as well as long-term (decadal) shifts in precipitation, a problem recently described by Hartmann et al., (2014).

2 Study Site

The Ichetucknee springs complex discharges from an unconfined portion of the upper Floridan aquifer, which represents an eogenetic karst aquifer in north-central Florida (Figure 1a). The complex contains 8 named springs that range between first and third magnitude (>2.8 to $0.028 \text{ m}^3/\text{sec}$, Meinzer, 1927) and numerous unnamed smaller springs and seeps (de Montety et al., 2011; Kurz et al., 2013; Kurz, 2015) and form the entirely spring-fed Ichetucknee River. The upper Floridan aquifer is eogenetic, with matrix porosity values of around 20 to 30% (Budd and Vacher, 2004). The upper Floridan aquifer is confined by Miocene Hawthorn Group rocks in the northern portion of the Ichetucknee springshed (e.g., the recharge area of the springs), which includes approximately 960 km^2 of the Santa Fe River watershed in north-central Florida (Fig. 1b). The confined and unconfined upper Floridan aquifer is bounded by the erosional edge of the Hawthorn Group, referred to as the Cody Scarp (Scott, 1988; Scott, 1992). At this boundary, all surface streams sink into the subsurface, limiting the presence of surface water in the springshed to karst windows (e.g., sinkholes) and Ichetucknee and Santa Fe rivers (Fig. 1c). Rainfall averages around 1300 mm/yr with a bimodal distribution; about half the annual precipitation falls between May and October as convective thunderstorms and tropical storms (Schmidt et al., 2001). This normal dry-wet cyclicity changes with oscillations in global climate, such as the ENSO and AMO, in which rainfall intensity during the winter months may increase in northern Florida, depending on the phases of the two cycles (Goly and Teegavarapu, 2014; Keener et al., 2010; Mitra et al., 2014).

Extensive previous work has been conducted on the Ichetucknee springs and river as the ecosystem has shifted from macrophyte to algal dominated (Stevenson et al., 2007). This shift corresponds with an increase in NO_3 concentrations, although questions remain about linkages between the NO_3 increase and alteration of ecosystems (Heffernan et al., 2010). The springs are

mostly chemostatic {Nifong, 2014 #1931}, but two groups of springs are recognized based on differences in dissolved oxygen (DO) concentrations and temperature (Martin and Gordon, 2000). Group 1 springs (Head and Cedar) have higher DO concentration and more variable temperatures than Group 2 springs (Mission, Devil's Eye, and Mill Pond), suggesting shallower flow paths. The sixth spring sampled in this study, Blue Hole Spring, was not classified by Martin and Gordon (2000), but based on DO, Mg, and SO₄ concentrations we assign Blue Hole Spring to Group 1.

Apparent ages range from around 10 to 50 years at numerous springs across Florida based measured on CFC, ³H/³He, and SF₆ tracers in samples collected between August 1998 and January 2003 (Happell et al., 2006; Katz, 2004; Katz et al., 2001). At three of the Ichetucknee springs (Head, Blue Hole, and Mission springs) apparent ages range from 13.8 to 42.5 yrs and average 26.1 yrs (Table 1) based on ³H/³He, CFC-11, CFC-12, and CFC-113 tracers. Although these previously published data have a wide range, the CFC apparent ages at Head Spring, a Group 1 spring, are mostly younger than those obtained from Mission Spring, a Group 2 spring (Table 1).

3 Methods

3.1 Field sampling and data mining. Flow data were compiled from the USGS gauging station 02322688 at Blue Hole Spring and for the Ichetucknee River from the USGS gauging station 02322700 at the US 27 bridge (Fig. 1c). We use these data as a proxy for spring discharge conditions. Monthly precipitation data were compiled from the Florida Climate Center (<http://climatecenter.fsu.edu/products-services/data>) from 1960 through 2014 for the city of Gainesville (the nearest long-term precipitation record) approximately 40 km southeast of the study area. Monthly rainfall, averaged over the period of record, P_{ma}, was calculated and the

measured rainfall for each month, P_m , was subtracted from the average to estimate the relative monthly excess or deficit rainfall P_{ed} for that month:

$$P_{ed} = P_{ma} - P_m \quad (1)$$

The excess and deficit were summed by month starting in 1960 to estimate a cumulative excess and deficit, P_c :

$$P_c = \sum_{t=1960}^{2014} P_{ed} \quad (2).$$

Water samples ($n=27$) were collected from six of the Ichetucknee springs (Head, Cedar, Blue Hole, Mission, Devil's Eye, and Mill Pond springs) on September 2, 2009, July 27, 2012 and August 2, 2013 and, additionally, from three of these springs (Head, Blue Hole, and Mill Pond springs) on October 25, 2012, February 14, 2013, and May 16, 2013 (Fig. 2). The 2009 sampling occurred during low flow and the 2012-2013 sampling occurred during the flood recession following Tropical Storm Debby.

Water was collected and preserved for major element and NO_3 concentrations and apparent age tracers, including CFCs, SF_6 , and $^3\text{H}/^3\text{He}$. Water was pumped into an overflow cup using a Geotech peristaltic pump at flow rates of ~ 1 L/min by extending flexible PVC tubing from the bank to ~ 1 m below the spring boil using rigid PVC rods. The overflow cup contained probes attached to a calibrated YSI 556 multi-parameter meter (Yellow Springs Instruments, Yellow Springs, Ohio), which measured DO concentrations, temperature, specific conductivity, and pH. Water was pumped until all the measured parameters stabilized, typically after about 5

minutes, and then filtered into two 20 ml HDPE bottles using in-line, trace-metal grade, $0.45\mu\text{m}$ canister filters. One 20 ml bottle had been acid washed in the laboratory and this sample, which was preserved with trace-metal grade HNO_3 , added drop wise until the $\text{pH} < 2$, was used for measurement of major cation concentrations, of which only Mg is reported here. The other 20-ml sample was used to measure major anion concentrations, of which only SO_4 concentrations are reported here. In addition, water was collected in a 60 ml HDPE bottle for measurements of NO_3 concentrations. Water for measurements of NO_3 and major anion concentrations, were left unpreserved. All containers were triple-rinsed with sample water prior to filling. Samples were kept chilled on ice while in the field and during transport to the laboratory. The major element samples were refrigerated at 4°C and the NO_3 samples were frozen until measured. Samples were measured within a month of collection.

Water was collected for apparent age tracers following US Geological Survey (USGS) protocols (<http://water.usgs.gov/lab/>). Collection for $^3\text{H}/^3\text{He}$ ratios involved pumping water through an ~ 1 m length of 0.5 cm diameter Cu tubing for one minute while tapping the outside of the tubing to dislodge air bubbles. After all air bubbles were removed, the outlet end of the tubing was crimped shut to elevate pressure in the tube to prevent introduction of air. The inlet end of the tube was crimped as soon as flow stopped. Each sample was collected in duplicate. For the analyses of CFC and SF_6 concentrations, 1 L glass bottles with ground glass tops were filled from the bottom and allowed to overflow into a secondary plastic bottle with a screw top. After both the glass and plastic bottles were filled, tops were installed on the interior glass bottle and clamped while keeping the bottle submerged. The glass bottle was then inverted in the plastic bottle, which was refilled to the brim with spring water. The top was screwed in place and sealed with electrical tape.

205 **3.2 Sample analyses.** Magnesium, SO₄, and NO₃ concentrations were measured at the

206 University of Florida using an automated Dionex DX500 ion chromatograph (supplemental
207 data). Errors of the measurements are < 3% based on 1 σ of repeated measurement of internal
208 check standards measured every fifth sample.

209 All of the tracer concentrations were measured at the Lamont-Doherty Earth Observatory
210 Environmental Tracer Laboratory (<https://www.ldeo.columbia.edu/environmental-tracer-group>).

211 The ³H and tritiogenic helium (³He_{trit}) analyses were measured on automated VG5400 mass
212 spectrometers dedicated to each isotope. The analytical error for ³H is 3.5% (1 σ) and for ³He_{trit}
213 is 1.4% (1 σ) when averaged for all samples included in the study. Neon concentrations were
214 measured on the same instrument to calibrate for contamination with air. Ages were corrected
215 for ³He_{trit} when necessary. The ³H/³He ratios were used to calculate apparent ages by the Tracer
216 Environmental Group at Lamont Doherty Earth Observatory (Schlosser et al., 1988). The SF₆
217 and CFC concentrations were measured with gas chromatography using electron capture
218 detectors. Errors were estimated as differences between duplicate samples, which vary from
219 2.1% for CFC-12 (range 0.4 to 8.7%), 8.3% for CFC-11 (range 0.1 to 33.8%) and 10.2% for
220 CFC-113 (range 0 to 43.9%).

221 **3.3 Data analyses.** Several approaches have been used to assess tracer ages, but the most
222 common approach, and the one we use, is through lumped parameter models (Maloszewski and
223 Zuber, 1996; Turnadge and Smerdon, 2014). Assuming no radioactive decay or biodegradation,
224 tracer concentrations at the spring can be simulated based on their input history using a
225 convolution integral

$$C_{out}(t) = \int_{-\infty}^t C_{in}(t')g(t - t')dt' \quad (3)$$

(Jurgens et al., 2012) where $C_{out}(t)$ is the tracer concentration at the spring, $C_{in}(t')$ is the concentration of the recharged tracer at time t' when the water recharged the aquifer, t is the sampling time, $t-t'$ is the age of the water parcel, and $g(t-t')$ represents an “exit age function” that describes the apparent age distribution in a water sample. The mean age of the sample, τ_s , composed of multiple water parcels is derived from equation 3 by:

$$\tau_s = \int_{-\infty}^t (t - t') g(t - t') dt \quad (4)$$

which can be approximated by:

$$\tau_s = \sum_{i=1}^{\infty} t_i X_i(\Delta t) \quad (5)$$

where t_i is the age of an individual water parcel, X_i is the fraction of each water parcel, and Δt is the time step.

Multiple models may be used to estimate the age distribution of a sample; here we use the lumped parameter model TracerLMP (Jurgens et al., 2012) to calculate ages using the piston flow model (PFM), exponential mixing model (EMM), and dispersion model (DM). These models assume an average recharge temperatures of 22° C, similar to those estimated for Ichetucknee springs by Heffernan et al. (2012). Each model was calculated for all samples with single CFC concentrations, all pairs of CFC concentrations (CFC-11 and -12, CFC-11 and -113, and CFC-12 and -113), as well as all three CFC tracers simultaneously. Consequently, each of the 53 samples (27 samples collected in duplicate, with one lost) measured for this study yielded

7 unique model apparent ages: a value for each of the three CFC tracers, three possible pairs of tracers, and the three tracers when combined. Each of these ages was evaluated using each of three model types for a total of 1113 realizations. Parameters utilized in TracerLMP include apparent age constraints ranging from 10 to 50 years, based on the apparent ages reported previously (e.g., Table 1). Binary mixing models (BMM) were evaluated assuming mixing between water with apparent ages calculated by the PFM, EMM, and DM. Apparent ages were also calculated from the USGS Report 2020 excel spread sheet (http://water.usgs.gov/lab/software/USGS_CFC/), which uses a PFM constrained by the SIO 2020 CFC concentration data.

4 Results

4.1 Precipitation, flow, and major element chemistry. The first samples were collected in 2009 during a low flow period with river discharge of $7.2 \text{ m}^3/\text{sec}$ (Fig. 2). Additional samples were collected approximately every three months after Tropical Storm Debby deposited 342 mm of rain in the Ichetucknee springshed between June 24 and 26, 2012. Discharge increased to $20 \text{ m}^3/\text{sec}$ four days after storm and then decreased to $7.5 \text{ m}^3/\text{sec}$ a week later. The initial peak discharge may be an artifact of back flooding of the Santa Fe River, which disrupts the rating curve for the Ichetucknee River. Discharge reached a local maximum of $11.0 \text{ m}^3/\text{sec}$ on July 29, 2012, two days after our initial post-storm sampling event, followed by a second maximum of $11.4 \text{ m}^3/\text{sec}$ on August 27, 2012. Discharge declined steadily to a minimum of $6.9 \text{ m}^3/\text{sec}$ on March 8, 2013. Samples were collected three times during this recession. Discharge was variable over the next couple months but rose to $14 \text{ m}^3/\text{sec}$ on August 6, 2013 after 565 mm of precipitation fell between June and August 2013 and four days following our final sample collection (Fig. 2).

The DO, NO₃, SO₄ and Mg concentrations vary little through time at individual springs, but vary significantly between the two spring groups (Table 2). Group 1 springs have higher DO and NO₃ and lower Mg and SO₄ concentrations than the Group 2 springs, similar to results reported in Martin and Gordon (2000). The values of the mean concentrations are 35.3 and 5.9 mg/L for DO, 0.053 and 0.021 mM for NO₃, 0.07 and 0.28 mM for Mg, and 0.23 and 0.4 mM for SO₄ for Group 1 and Group 2 springs, respectively. Based on Student's t-test analyses, these means are different at a significance of $p < 0.001$.

4.2 Flow models and apparent ages. The PFM shows more consistent apparent ages than the EMM or DM, similar to previous models of apparent ages in the Floridan aquifer (Happell et al., 2006; Katz, 2004; Katz and Hornsby, 1998). The EMM found apparent ages that differed by an average of 76 yrs for individual samples, depending on tracers used, to a maximum of 373 yrs for the May 16, 2013 Mill Pond sample (88.1 yrs with CFC-12 and 461 yrs combining CFC-11, CFC-12, and CFC-113). The DM found apparent ages greater than 50 years for 146 realizations and required dispersion parameters ≤ 0.1 for 173 realizations (of 361). At a dispersion parameter of 0, the DM is identical to the PFM (Jurgens et al., 2012) and below 0.1 the apparent ages are identical whether estimated from the DM and PFM. No BMM of the EMM, DM, or PFM was found to satisfy all constraints imposed on the models, including mixing fractions that ranged from 0.1 to 0.9 and ages of 1 to 5 years for the youngest waters.

Apparent ages from the PFM showed no difference when calculated using CFC data modeled with TracerLMP (Jurgens et al., 2012) and the USGS2020 spreadsheet. For Group 1 springs, the average apparent age ranged from 30.6 years for CFC-113 to 35.1 yrs for CFC-12 and was 32.1 years based on ³H/³He ratios (Table 2). For Group 2 springs, the average apparent age ranged from 37.5 yrs based on CFC-113 concentrations to 41.4 yrs based on the CFC-11

ages and was 32.0 yrs based on the $^3\text{H}/^3\text{He}$ ratios. Except for Head Spring, measured SF_6 concentrations were higher than possible based on known atmospheric SF_6 concentrations (e.g., Busenberg and Plummer, 2000). Equilibrium concentrations are 1 to 6×10^{-10} atm (up to 668 pptv) based on the algorithm reported in Bullister et al. (2002) while maximum atmospheric SF_6 concentrations were around 4 pptv (Busenberg and Plummer, 2000). For Head Spring, SF_6 concentrations yielded apparent ages of 4 to 43 yrs with an average apparent age of 12.5 yrs. Except for one apparent age of 43 yrs, all other estimated apparent ages are < 15 yrs, younger than apparent ages reported previously (Happell et al., 2006; Katz, 2004; Katz and Hornsby, 1998) or found here with other tracers.

4.3 Comparisons of apparent ages from CFCs and $^3\text{H}/^3\text{He}$. No correlation exists between apparent ages based on $^3\text{H}/^3\text{He}$ and all three CFC tracers (Fig. 3). The best correlations occur between the $^3\text{H}/^3\text{He}$ and CFC-12 and CFC-113 apparent ages at Head Spring, although several outliers occur in data from this spring as well (Fig. 3B and C). Apparent ages are mostly younger when evaluated from $^3\text{H}/^3\text{He}$ ratios rather than CFC concentrations in Blue Hole, Mill Pond, Mission, and Devil's Eye springs, but are older in Head and Cedar springs. These groupings of springs do not correspond to the groupings based on DO concentrations and temperature; Blue Hole and Head springs are in Group 1; while Mill Pond and Mission springs are in Group 2 (Table 2).

In contrast, significant correlations ($p < 0.0001$) exist in apparent ages of the three CFC tracers (Fig. 4) using our data alone and including previous data (Happell et al., 2006; Katz, 2004; Katz and Hornsby, 1998). Slopes of these correlations vary depending on which tracers are compared and the data included (Table 3). The slopes are near 1 only for regression analyses of CFC-113 and CFC-11 with our data and of CFC-12 and CFC-11 with all available data.

Slopes are < 1 (0.57) for regression analysis of CFC-113 and CFC-11 using all available data. Slopes of all other regression analyses are > 1 . These results indicate that CFC-113 estimates younger apparent ages relative to CFC-12 and CFC-11, particularly when all data are included in the analyses.

4.4 Comparisons between apparent ages and major element concentrations. The CFC apparent ages co-vary with DO, NO₃, Mg, and SO₄ concentrations. Apparent ages show inverse relationships with DO and NO₃ concentrations (Fig. 5). In contrast, apparent ages have a positive relationship with Mg and, to a lesser extent, SO₄ concentrations (Fig. 6). The best relationships between solute concentrations and apparent ages occur for samples from this study, while most samples collected between 1997 and 2003 (Happell et al., 2006; Katz, 2004; Katz et al., 2001), have younger apparent ages for solute concentrations similar to ours.

5 Discussion

5.1 Assessment of tracers used to estimate apparent ages. Excess SF₆ in our samples is unsurprising considering regional SF₆ contamination was reported previously (Katz, 2004), potentially from its use in the 1990s as an injected flow tracer (Catches, 1997; Hisert, 1994). The Santa Fe River watershed is largely agrarian, suggesting industry, one of the most common sources of SF₆ (Darling et al., 2012), is an unlikely contaminant source. The upper Floridan aquifer contains little fluorite and therefore this natural source (Harnisch and Eisenhauer, 1998) is also unlikely. Regardless of source, contamination inhibits quantitative analyses of apparent age from SF₆ (e.g., Busenberg and Plummer, 2000); however, if excess SF₆ resulted from injections in the 1990s, its presence two decades later suggests minimum residence times on the order of decades. These residence times qualitatively supports observations of apparent ages of several decades from ³H/³He and CFC data (Fig. 3).

The incongruence of CFC and $^3\text{H}/^3\text{He}$ apparent ages suggests one or both were altered during atmospheric equilibration or after recharge (Fig. 3). The incongruence is unlikely a result of equilibration temperature, which we estimate to be a constant 22° C, identical to Heffernan et al. (2012) because the small temperature range in north Florida has little affect on apparent ages. Analytical error of the $^3\text{H}/^3\text{He}$ ages is also unlikely to cause the incongruences; uncertainties were less than 2.5 year at apparent ages of about 40 years in an intercalibration experiment between 14 laboratories (Visser et al., 2014). Uncertainty may also originate from presence of non-tritiogenic ^3He (Visser et al., 2014). An important source of non-tritiogenic ^3He is from the mantle in tectonically active settings (Mahara et al., 2014), although this source is not expected in most aquifers (e.g., Schlosser et al., 1988), including the tectonically stable karstic Florida platform. Nonetheless, terrigenic ^3He was found in several Florida springs as a result of mixing older water with elevated $^3\text{He}/^4\text{He}$ ratios (Happell et al., 2006). Where the vadose zone is thin in karst regions of Burgundy France, He and Ne concentrations were found to be close to atmospheric values, suggesting re-equilibration with the atmosphere, although the samples contained little excess air (Delbart et al., 2014). Similar modifications could occur in the Floridan aquifer because of its elevated porosity, and a vadose zone only a few meters thick, which is composed mostly of unconsolidated Plio-pleistocene quartz sands (Moore et al., 2009; Scott, 1988; Scott, 1992). Noble gases are more prone to re-equilibration than CFCs because of their more rapid diffusivity (Han et al., 2006; Jähne et al., 1987; Schlosser et al., 1989).

The CFCs appear to provide the most accurate apparent ages considering their congruent behavior (Fig. 4); however, CFC concentrations may also be modified by several processes, including analytical uncertainty, variations in ambient recharge temperature, vadose zone processes, contamination in the subsurface, and non-conservative behavior during flow through

and reactions with the aquifer material (Busenberg and Plummer, 1992; Cook et al., 2006). Analytical uncertainty for CFCs is on the order of a couple of years based on an intercalibration experiment (Labasque et al., 2014), and thus unlikely to cause incongruent ages with $^3\text{H}/^3\text{He}$ (Fig. 3). CFC-11 may be retarded relative to CFC-12 in regions where thick vadose zones allow interactions of the CFC with soils (Busenberg and Plummer, 1992; Weeks et al., 1982), but this process is unlikely in the Santa Fe River watershed because of its thin overburden and vadose zone (Moore et al., 2009; Scott, 1988; Scott, 1992). The agrarian land use in the region should limit industrial or septic contaminations (e.g., Cook et al., 2006).

Since slopes of correlations between the different CFCs are not equal and some differ from one, alterations may be distinct for each CFC. Alteration most commonly occurs from biodegradation in anoxic aquifers (Busenberg and Plummer, 1992; Semprini et al., 1992). Of the three CFCs, CFC-11 is the most susceptible to degradation, particularly as the redox state of aquifers approach sulfate reduction (Cook et al., 2006; Katz et al., 1995). For example, CFC-11 concentrations decreased by 68%, while CFC-113 decreased by 20% and CFC-12 was unaltered during a biostimulation experiment under anoxic conditions (Semprini et al., 1992). CFC-12 was also found to be the most conservative of the three CFCs in a sandy-silty aquifer in Ontario where CFC-11 and CFC-113 were retarded and CFC-11 was degraded where oxygen was < 0.5 mg/L (Cook et al., 1995). CFC-11 was found to be degraded in the upper Floridan aquifer north and west of our field area while CFC-12 yielded robust apparent ages (Katz et al., 1995; Plummer et al., 1998a; Plummer et al., 1998b).

All of the Group 1 springs and most of the Group 2 springs contain more oxygen than the 0.5 mg/L threshold for degradation (Fig. 5) and no sulfate reduction, suggesting major CFC degradation is unlikely. Minor degradation may occur in the Group 2 springs, which contain less

oxygen than Group 1 springs and may result in the older apparent ages for Group 2 than Group 1 springs (Fig. 5). The young apparent ages based on CFC-113 relative to CFC-12 (Fig. 4; Table 3) could represent degradation because CFC-12 is less susceptible to degradation than CFC-113. An alternate explanation for the young apparent ages based on CFC-113 may be from enrichment from contamination, the most likely being septic systems within the watershed. Contamination of CFCs were found in 12 of 31 Florida springs sampled by Happell et al. (2006), but the contaminated samples were located near large urban areas, and no contamination was found at Ichetucknee Head Spring in that study. Similarities in apparent ages derived from all three CFCs suggest they provide the best apparent age for discharging water and therefore the following discussion focuses on CFC apparent ages.

5.2 Flow models. Models used to interpret apparent ages include mixing cell models, direct age models and lumped parameter models (see review in Turnadge and Smerdon, 2014). The first two models represent discretization of aquifers that allow numerical solutions to calculate mean groundwater age (mixing cell models) or solute transport equations (direct age models). Lumped parameter models, which use a regression approach to develop solutions to equation 5, are most common (Turnadge and Smerdon, 2014) and are particularly useful for karst aquifers because of their heterogeneous permeability (e.g., Long and Putnam, 2006; Long and Putnam, 2009). Apparent ages of upper Floridan aquifer water were evaluated previously with lumped parameter models (Happell et al., 2006; Katz, 2004; Katz et al., 2001; Katz et al., 1999), which we duplicate here to estimate comparative apparent ages from our new CFC data. For lumped parameter models, three exit age functions [e.g., $g(t-t')$ in equation 5], specifically PFM, EMM, and DM, can be used to evaluate apparent ages depending on characteristics of the aquifer. Spatial distributions of these models also allow for hybrid models (Jurgens et al., 2012;

Maloszewski and Zuber, 1996; Plummer et al., 2006). We assume a PFM here, since the PFM yielded coherent apparent ages for 47 springs across Florida but inconsistent apparent ages with the EMM (Happell et al., 2006; Katz et al., 2001). The only realistic solutions to the DM required dispersion coefficients low enough to mimic the PFM. The assumption of a PFM suggests the high matrix porosity and permeability affects a large portion of flow in the eogenetic karst in the upper Floridan aquifer (e.g., Florea and Vacher, 2006; Florea and Vacher, 2007)

Piston flow could be complicated by binary mixing between various recharge events, a process identified at some Florida springs (Katz et al., 2001), but our data suggest no binary mixing occurs at Ichetucknee springs, even following Tropical Storm Debby. The lack of binary mixing could indicate storm water represents a fraction of the discharge water only within days of the storm. Groundwater flow rates to Ichetucknee springs have been found to be on the order several kilometers per day based on dye trace results (Wilson and Skiles, 1988) and based on decreased SO_4 and increased NO_3 concentrations at the normally chemostatic Mill Pond Spring 8 days following a single 237 mm rain event (Martin and Gordon, 2000). Rapid flow into and from the upper Floridan aquifer is observed when flooding causes intrusion of river water into some Florida springs followed by discharge of the flood water within a few days to weeks (Gulley et al., 2011; Kincaid, 1998). These results suggest much water recharged during Tropical Storm Debby may have discharged by quick flow prior to our sampling, such that the fraction of storm water in our samples was below analytical resolution.

5.3 Analyses of solute-age relationships. Temperature gradients in monitoring wells approximately 10 km east of Ichetucknee springs indicate that Floridan aquifer water flows upward from a depth of approximately 400 m below the water table to discharge from the Santa

Fe River Rise, a nearby first magnitude spring that represents the headwaters of the lower Santa Fe River (Jin et al., 2014; Moore et al., 2009). This upward-flowing water is characterized by low oxygen (< 0.5 mg/L), and elevated Mg, and SO_4 concentrations. These compositional changes result from oxidation of organic carbon and dissolution of gypsum in the Paleogene Avon Park Formation (e.g., Scott, 1992), which reduces oxygen concentrations, elevates SO_4 concentrations, causes dedolomitization, and increases Mg concentrations (Moore et al., 2009). Elevated Mg and SO_4 concentrations coupled with low DO concentrations in Group 2 springs compared with Group 1 springs (Fig. 5) suggests the Group 2 springs contain more of this deep water source than the Group 1 springs. The Group 2 springs tend toward older apparent ages than springs with elevated DO concentrations, supporting the conclusions of Martin and Gordon (2000) that springs with low DO concentrations discharge from long, deep flow paths. Although only four samples are available with elemental data for water collected between 1997 and 2001, these samples also reflect older apparent ages in Group 2 springs than the Group 1 springs (Table 2), indicating flow paths to both spring groups have not varied over decadal time scales. In addition to similarities in the deep water source identified by Moore et al., (2009), Group 2 springs also have average $^4\text{He}_{\text{terr}}$ concentrations ($4.9 \text{ cm}^3 \text{ STP/g}$) that are significantly higher ($p < 0.001$) than the Group 1 springs ($1.6 \times 10^{-8} \text{ cm}^3 \text{ STP/g}$). The elevated $^4\text{He}_{\text{terr}}$ concentrations also reflect greater amount of water-rock reactions of water resulting from longer flow paths for Group 2 than Group 1 springs (e.g., Morgenstern and Daughney, 2012).

Nitrate is a contaminant of concern in the Floridan aquifer and thus numerous studies have assessed the relationship between NO_3 concentrations and apparent ages regionally across the upper Floridan aquifer (Katz, 2004; Katz et al., 2001; Katz et al., 2004; Katz et al., 1999) but none has evaluated how NO_3 concentrations vary with apparent age of the water through time.

Our data show an inverse relationship between NO_3 concentrations and apparent age of Ichetucknee spring water (Fig. 5B). Regression analyses of these data show statistically significant slopes ($p < 0.0001$) of $-0.0022 \text{ mM-NO}_3/\text{yr}$ for the CFC-11 apparent age ($r^2 = 0.63$), $-0.0029 \text{ mM-NO}_3/\text{yr}$ ($r^2 = 0.61$) for the CFC-113 apparent age to $-0.0055 \text{ mM-NO}_3/\text{yr}$ ($r^2 = 0.89$) for the CFC-12 apparent ages. Y-intercepts for the linear regressions range from 0.12 to 0.23 mM-NO_3 . The four samples reported by Katz (2004) and Katz et al. (2001) that were collected between 1997 and 2001 show similar slopes and y intercepts for regression analyses of NO_3 concentrations and CFC-11 and CFC-12 apparent ages ($p < 0.001$), but the relationship between NO_3 concentrations and CFC-113 apparent ages are not statistically significant. The cause for this lack of correlation is unknown.

The inverse relationship of apparent age and NO_3 concentrations (Fig. 5B) may reflect loss of NO_3 from the upper Floridan aquifer, presumably from denitrification since other processes such as assimilation and dissimilatory nitrate reduction to ammonium are negligible (Heffernan et al., 2012). Assuming that the amount of denitrification decreased at a linear rate since recharge, the y-intercepts reflect initial NO_3 concentrations of between 0.12 and 0.23 mM , or approximately 0.5 to 3 times higher than estimates made by Heffernan et al. (2012) that were based on the assumption that the Head Spring water had no denitrification. This difference could reflect some denitrification in the Head Spring water, considering its apparent age is on the order of several decades, although it should have the lowest amount of denitrification of all the springs as it has the youngest apparent age. Alternatively, our assumption of linear decrease in the amount of denitrification through time may not be valid. The amount of denitrification may decrease as electron donors, particularly labile organic carbon, are consumed during flow. Changes in denitrification rates are suggested by the generally similar NO_3 concentrations from

samples collected from 1997 to 2001 and our samples, even though the early samples have younger apparent ages, allowing for less time for denitrification to occur (Fig. 5B).

5.4 Possible causes of apparent age variations through time and implications. To our knowledge, this analysis is the first to evaluate apparent ages over a time period similar to the apparent age; specifically, Ichetucknee springs water apparent ages ranged from around 20 to 40 years over the 16 year study period. Our results show a monotonic increase in apparent age through the study with little rapid response following the large amount of precipitation caused by Tropical Storm Debby (Fig. 7), even though discharge was affected (Fig. 2). This result indicates that discharging groundwater was sequestered in the aquifer for periods of time prior to responding to the large precipitation event and associated elevated recharge. This behavior reflects paradox 1 described by Kirchner (2003), which is consistent with the PFM. The only other similar time-series study of apparent age occurred over a period of four years, when apparent ages of 16 to 33 years were found at Troy Spring (Florida), with apparent ages increasing from the first to final two years (Katz, 2004; Katz et al., 1999). This shift in age was interpreted to reflect a drought that occurred at the end of sampling, reflecting an immediate impact on discharge of previously recharged water. In contrast, the long term monotonic increase in apparent age at the Ichetucknee springs, and limited response to Tropical Storm Debby, suggests long-term changes in recharge are required to manifest themselves at springs, perhaps from slow flow through the elevated matrix porosity of eogenetic karst (e.g., Martin and Dean, 2001).

These long-term changes can be quantified for the three springs for which long time series results are available, specifically Head, Blue Hole and Mission springs. Regression analyses show linear increases with r^2 values > 0.89 ($p < 0.005$) for CFC-12 and CFC-113

apparent ages (Table 4). The average rates of change for the CFC-12 and CFC-113 apparent ages are 0.58 and 0.93 yr/yr for Head and Blue Hole springs (Group 1) and 0.33 yr/yr, or 2 to 3 times slower, for Mission Spring (Group 2). These differences suggest that Group 1 spring water may be more responsive to environmental conditions than Group 2 springs, a characteristic that would be expected based on their short and shallow flow paths (Martin and Gordon, 2000). Many telegenic karst systems are characterized by quick flow of storm water and rapid response to recharge events (Iqbal and Krothe, 1996; Lakey and Krothe, 1996; Meiman et al., 1988; Toran and Reische, 2012), while eogenetic karst springs have been found to respond to storms on the order of months (Florea and Vacher, 2006; Florea and Vacher, 2007). Longer time-scale changes of apparent age, for example at the scale of decades (e.g., Fig. 7), may include variations in recharge from climate cycles such as ENSO or AMO or from anthropogenic effects such as increased pumping (e.g., Hartmann, 2014 #2263).

Linkages between apparent age and climate cycles may be evaluated by comparisons with historic records of precipitation (Fig. 8). Apparent ages indicate average recharge dates of around 1980 (± 2.4 yrs; 1 σ) for Group 1 springs and around 1973 (± 2.8 yrs; 1 σ) for Group 2 springs for samples collected post Tropical Storm Debby. For samples collected between 1997 and 2003, apparent ages indicate average recharge dates of around 1980 for Group 1 springs (n = 8) and around 1979 from the Group 2 spring (n=2) (Table 1). All of these recharge dates correspond to the end of an approximately 15-yr period (1960 to 1975) when cumulative monthly rainfall (eq. 2) provided approximately 2 m of excess rain (Fig. 8B). Between 1980 and 2000, the cumulative monthly rainfall dropped to around 0.7 m and then decreased to around -2 m between 2000 and 2014 relative to 1960. The increased recharge resulting from the excess rainfall from 1960 to 1980 appears to remain the main source of water discharging from

Ichetucknee springs, as reflected in the similar recharge dates for samples collected between 1997 and 2013.

Decadal-long changes in precipitation correspond to global climate patterns, such as ENSO and AMO, which in the southeastern US increase precipitation during El Niño years (referenced to NINO 3.4 index of SST), particularly during cool phases (e.g., negative AMO index) of the AMO (Goly and Teegavarapu, 2014). These correspondences are shown by statistical correlations between precipitation and El Niño cycles, stream flow and nutrient distributions in southern Georgia (Keener et al., 2010), stream flow in the Suwannee River (Tootle and Piechota, 2004), numerous smaller watersheds in west-central Florida south of our field area (Risko and Martinez, 2014), and shifts in precipitation between northern and southern Florida during the cool period of the AMO (Enfield et al., 2001), in part from changes in summer convectional and tropical storms in the south to winter frontal systems in the north (Schmidt et al., 2001). These changes in precipitation and stream flow also affect groundwater tables, which were found to be higher than average during El Niño phase and lower than average during La Niña phase (Mitra et al., 2014). Regardless of these climatological events, to our knowledge, no links have been reported previously to spring discharge in the southeastern US, although Idaho spring discharge has been shown to reflect the Pacific Decadal Oscillation and El Niño (Harshburger et al., 2002).

The most recent cool period of the AMO extended from 1960 to 1995, with the maximum negative AMO index between 1970 and 1980 (Fig. 8). Strong El Niño years occurred in 1973-1974 and 1983-1984, around the time apparent ages indicate enhanced recharge. The coincidence between El Niño, AMO and apparent age suggests that water currently discharging from Ichetucknee springs is weighted toward having been recharged during periods of excess

precipitation resulting from these global climate patterns. Once excess precipitation decreased, the Ichetucknee springs appear to have begun to discharge upper Floridan aquifer water that had been stored for increasingly long times. Predicting future coincidence of an AMO cool period and El Niño, and, thus, the reversal in the current cumulative precipitation trend, is complicated by the long periodicity of the AMO cycle and limited number of cycles that have been observed to date.

Alternatively, our observations of apparent ages increasing through time could result from increased anthropogenic withdrawal of groundwater. Withdrawal volumes of water are unavailable for the Ichetucknee springshed but are estimated for individual counties and water management districts (multi-county). We downscale the county and district wide values to the Ichetucknee springshed area to estimate volumes of withdrawal relative to discharge of Ichetucknee River. The springshed is contained almost entirely within Columbia County, which covers 2075 km². Groundwater withdrawal in Columbia County was 0.6 m³/sec in 2010 (Marella, 2014) which represents about 2.5 to 5% of the total flow in the Ichetucknee River, assuming about half of this withdrawal came from the 960 km² Ichetucknee springshed. The Ichetucknee springshed is within the 19,619 km² Suwannee River Water Management District for which water withdrawals are regularly estimated. These withdrawals remained flat or declined slightly for all sources between 1950 and 2010, except for agricultural self-supply, which increased from about 1 m³/sec to 5.5 m³/sec (Marella, 2014). Assuming this withdrawal is uniform across the district, approximately 0.05 to 0.27 m³/sec of water would have been withdrawn from the Ichetucknee springshed during 2010. This withdrawal represents about 0.3 to 4.5% of the total flow, similar to the estimates based on water extraction from Columbia County. Although water withdrawal must impact changes in flow, and thus the apparent age of

water discharging from the Ichetucknee springs, the larger affect seems to be from changes in precipitation, which correspond to changes in global climate patterns.

A finite amount of water recharged the Ichetucknee springshed during the period of excess rainfall in the last cool cycle of the AMO. As this recharge is depleted through spring discharge and water withdrawal, discharge will increasingly draw from the limited recharge that occurred during the AMO warm period (Fig. 8). These deficits in recharge should also occur for the hundreds of springs across the region, many of which are experiencing declines in flows. These results indicate that managing and allocating groundwater resources for consumption and ecosystem use will become increasingly difficult as groundwater availability decreases. This relationship between recharge and discharge amounts, water consumption, and global climate patterns should occur worldwide for groundwater sources with similar hydraulic conductivity distributions where climate patterns vary systematically (e.g., Hartmann et al., 2014). Although these relationships should be particularly acute in karst aquifers because of their rapid response to flow and storage, similar relationships could occur in all types of aquifers.

6 Conclusions

Time-series variations in apparent ages indicate that water discharging from the Ichetucknee springs from 1997 to 2013 was recharged at a time coinciding with two major El Niño events and the maximum cool phase of the AMO between 1960 and 1980. During this period, around 2 m of excess rain fell in the region. Even a single large recharge event caused by Tropical Storm Debby in 2012 was insufficient to decrease the apparent age of spring water over the year-long recession from the event, although some recharge may have passed through the system in a matter of days after the storm and was not sampled. These results indicate that relative contributions from different flow paths did not change following the storm and instead

the storm remobilized old water. These results also indicate eogenetic karst aquifers are impacted by decadal long variations in precipitation in addition to well-known short term increases (e.g., days to months) in telogenetic karst caused by single large precipitation events (Florea and Vacher, 2007; Meiman et al., 1988; Shuster and White, 1972). Although decade-long variations in water withdrawal, which increased by about a factor of 5 between 1980 and 2005, may affect discharge from Ichetucknee springs, the magnitude this effect appears to be less than changes in rainfall related to global climate patterns. In addition to water quantity, water quality, particularly reactive components such as NO_3 and DO, also reflect apparent age, recharge times, and length of flow paths. For eogenetic karst aquifers that are less flashy than telogenetic aquifers, the long-term controls on flow patterns suggest contaminants are sensitive to long-term changes in recharge. These results indicate that eogenetic karst aquifers should be managed considering long-term global climate patterns. Understanding the relationships between global climate patterns and recharge, discharge, and effects of residence times of mineralization and contaminant remediation provides predictive capability for managing water withdrawal and usage.

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Figure Captions

Figure 1. A. Distribution of confined, semi-confined, and unconfined Floridan aquifer in north Florida (FDEP, 2006; modified). B. Digital elevation model of the Ichetucknee springshed outlined in white (SRWMD, 2007; modified). Elevated portion (red tones) reflects presence of Hawthorn Group rocks where the Floridan aquifer is confined. The white dashed line represents the springshed as delineated by Champion and Upchurch (2003). Diamonds represent sinkholes that capture runoff from confined unit. C. Google Earth image of Ichetucknee River showing the state park (white outline) and 6 sampled springs (blue stars), separated into Group 1 and Group 2. Modified from Kurz et al. (2013).

Figure 2. Times samples were collected (purple circles) for the project along with precipitation (collected by Suwannee River Water Management District), discharge from Blue Hole Spring (USGS gauging station 02322688) and at the US Highway 27 Bridge (USGS Gauging station 02322700). The large precipitation event in July 2012 occurred when Tropical Storm Debby crossed the region. Data compiled from the Suwannee River Water Management District.

Figure 3. $^3\text{H}/^3\text{He}$ ages versus A. CFC11 apparent age, B. CFC12 apparent age, and C. CFC113 apparent age. The diagonal lines represent a 1:1 correlation between the apparent ages determined from the $^3\text{H}/^3\text{He}$ and CFC ages.

Figure 4. Cross plots of apparent ages derived from CFC concentrations using the PFM. A. CFC-12 versus CFC-11, B. CFC-113 versus CFC-11, C. CFC-12 versus CFC-113. Data reported previously (Katz and Hornsby, 1998; Katz, 2004; Happell et al., 2006) are shown as open symbols and indicated by an asterisk in the legend. The solid lines represent a slope of 1. The dotted lines represent linear regressions with data from this study. The dashed lines represent linear regressions of data from this study as well as reported previously. Correlations of all linear regressions are statistically significant at $p < 0.0001$.

Figure 5. Cross plots of A. dissolved oxygen concentrations and B. NO_3 versus apparent ages estimated by CFC-11, CFC-12, and CFC-113. The filled symbols are new data from this study and the open symbols are data from Katz and Hornsby (1998) and Katz et al. (2004).

Figure 6. Cross plots of dissolved A. Mg and B. SO_4 concentrations versus apparent age as estimated by CFC-11, CFC-12, and CFC-113. The filled symbols are new data from this study and the open symbols are data from Katz et al., 1998; 2004.

Figure 7. Date of sample collection versus A. CFC12 apparent ages for Group 1 springs, B. CFC12 apparent ages for Group 2 spring, C. CFC113 apparent ages for group 1 spring, and D. CFC113 apparent ages for Group 2 springs versus the date of collection.

Figure 8. A. Oceanic El Niño index (ONI, black) and Atlantic Multidecadal Oscillation (AMO) index shown as a 12-month smoothed value (red). Positive values represent El Niño and warm AMO periods. Negative values represent La Niña and cool AMO periods. B. Cumulative rainfall for Gainesville. Arrows represent average apparent recharge time for both spring groups; width of arrowhead approximately 1σ variation in estimates.

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Table 1. Apparent ages of Ichetucknee springs from previous studies

Sample Location	Sampling Date (m/d/y)	Apparent Age ³ H/ ³ He		CFC-11*		CFC-12*		CFC-113*		Source
		(yr)	+/-**	(yr)	+/-	(yr)	+/-	(yr)	+/-	
Head	10/24/01	26.0	0.5	27.8	0.0	26.6	0.6	13.8	2.8	Katz, 2004
Head	01/04/03	42.5	N/A	29	N/A	28	N/A	25	N/A	Happell et al., 2006
Blue Hole	08/14/97	N/A	N/A	28	1	26	0	16	4	Katz and Hornsby, 1998
Blue Hole	10/24/01	24.1	0.5	32.8	0.0	25.0	6.3	17.3	1.3	Katz, 2004
Mission	10/24/01	23.4	0.5	33.8	0.3	34.0	0.3	17.1	0.8	Katz, 2004

* Recalculated based on USGS 2020 calculator.
** +/- reflects difference in duplicate values. Where missing, only single value was measured.

Table 2 – Major element concentrations and apparent ages from CFC concentrations (PFM) and $^3\text{H}/^3\text{He}$ ratios

	Sampling Location	(m/d/y)	DO (%)	DO (mg/L)	SO4 (mM)	Mg (mM)	Apparent Age $^3\text{H}/^3\text{He}$		CFC-11		CFC-12		CFC-113	
							(yr)	+/-	(yr)	+/-	(yr)	+/-	(yr)	+/-
Group 1 Springs	Head	09/03/09	38.5	3.4	0.08	0.23	30.3	0.6	24.2	1.0	32.7	0.0	27.2	0.0
	Head	07/27/12	44.3	3.9	0.09	0.24	32.9	0.6	31.1	0.0	33.6	0.0	29.6	0.0
	Head	10/25/12	39.5	3.5	0.09	0.25	32.5	0.4	30.3	0.0	34.6	0.5	29.3	0.0
	Head	02/14/13	40.4	3.5	0.09	0.25	36.7	0.4	31.1	1.0	34.1	0.0	31.1	2.0
	Head	05/16/13	50.2	4.4	0.09	0.25	33.2	0.4	30.9	1.0	34.1	0.5	31.6	0.5
	Head	08/02/13	45.0	3.9	0.09	N/A	34.5	0.5	21.8	0.5	34.1	0.0	32.3	0.5
	Cedar	09/03/09	26.1	2.3	0.06	0.21	47	0.7	35.7	0.0	35.2	0.0	30.2	0.0
	Cedar	07/27/12	32.2	2.8	0.06	0.23	35.3	0.8	36.6	0.0	36.6	0.0	29.6	0.0
	Cedar	08/02/13	31.5	2.7	0.06	N/A	35.8	0.7	32.8	3.5	36.8	0.5	32.8	0.5
	Blue Hole	09/03/09	20.8	1.8	0.06	0.21	35.3	0.7	27.4	4.5	35.4	0.5	28.4	0.5
	Blue Hole	07/27/12	19.6	1.2	0.06	0.23	28.1	0.7	38.1	0.0	36.1	0.0	30.3	0.5
	Blue Hole	10/25/12	31.8	2.8	0.06	0.23	25.6	0.3	36.1	2.5	36.1	0.5	29.3	0.0
	Blue Hole	02/14/13	38.1	3.4	0.06	0.23	25.6	0.3	37.6	0.0	35.1	0.0	33.4	0.5
	Blue Hole	05/16/13	35.8	3.1	0.05	0.23	26.8	0.4	37.9	0.0	35.4	0.0	30.4	0.0
	Blue Hole	08/02/13	35.2	3.1	0.05	N/A	22	0.6	29.8	1.5	36.3	0.5	33.1	1.0
	Average:		35.3	3.0	0.07	0.23	32.1	0.54	32.09	1.0	35.08	0.20	30.6	0.40
	1 σ		8.61	0.82	0.02	0.01	6.09	0.16	5.00	1.42	1.20	0.25	1.80	0.54
Group 2 Springs	Mission	09/03/09	1.9	0.2	0.15	0.31	36.8	0.7	40.9	0.5	38.2	0.0	34.9	0.5
	Mission	07/27/12	16.5	1.3	0.14	0.31	32.3	0.7	43.8	0.5	39.1	0.0	34.1	0.0
	Mission	08/02/13	7.5	0.7	0.11	N/A	N/A	N/A	36.1	1.9	38.9	1.4	36.1	7.9
	Devil's Eye	09/03/09	3.2	0.3	0.26	0.37	34.6	0.7	34.7	1.0	37.9	0.5	31.9	0.5
	Devil's Eye	07/27/12	4.1	0.4	0.26	0.39	30.6	0.7	42.8	0.5	40.1	0.0	34.3	0.5
	Devil's Eye	08/02/13	6.4	0.56	0.20	N/A	30.5	0.7	39.1	0.0	40.6	0.0	40.3	3.5

Mill Pond	09/03/09	1.8	0.2	0.44	0.43	32.3	0	38.7	1.0	40.9	0.5	37.2	0.0
Mill Pond	07/27/12	5.7	0.5	0.46	0.47	30.2	0.6	45.8	1.5	42.6	1.0	37.3	0.5
Mill Pond	10/25/12	5.7	0.5	0.41	0.45	31.3	0.3	44.1	0.5	41.8	0.0	38.3	0.0
Mill Pond	02/14/13	6.9	0.1	0.31	0.42	29.8	0.4	46.1	1.0	41.6	0.0	43.4	3.5
Mill Pond	05/16/13	4.5	0.4	0.31	0.41	31.2	0.4	43.9	0.0	41.9	0.0	44.1	2.5
Mill Pond	08/02/13	7.1	0.6	0.35	N/A	N/A	N/A	40.8	2.5	42.1	0.0	38.1	3.0
Average:		5.9	0.5	0.28	0.4	32.0	0.52	41.41	0.9	40.47	0.28	37.5	1.87
1 σ		3.85	0.34	0.12	0.06	2.20	0.24	3.68	0.75	1.62	0.48	3.68	2.36

Table 3. Regression analyses of CFC ages

Source of data	CFC comparison	slope	R²	Figure
This study	CFC12 v CFC 11	1.76	0.69	4a
This study	CFC113 v CFC11	1.01	0.49	4b
This study	CFC12 v CFC 113	1.26	0.75	4c
All	CFC12 v CFC 11	1.05	0.58	4a
All	CFC113 v CFC11	0.57	0.41	4b
All	CFC12 v CFC 113	1.41	0.82	4c

Table 4. Regression analysis, apparent age through time

Spring	tracer	n	R ²	p	slope (yr/yr)
Head	3H/3He	7	0.83	<.005	0.73
	CFC11	8	0.04	0.65	NA
	CFC12	8	0.97	<0.001	0.55
	CFC113	8	0.89	<.002	0.61
Blue Hole	3H/3He	7	0	0.97	NA
	CFC11	8	0.48	0.1	NA
	CFC12	8	0.92	<.001	0.76
	CFC113	8	0.96	<0.001	1.1
Mission	3H/3He	3	0.99	<0.001	0.31
	CFC11	4	0.99	<.005	0.36
	CFC12	4	0.99	<0.001	0.35
	CFC113	4	0.99	<0.001	0.31

NA = not applicable