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PECCI CODE (PYTHON™ ESTIMATION FOR CARBON CONCENTRATION AND ISOTOPES) FOR CALCULATING THE CONCENTRATION AND STABLE CARBON ISOTOPIC COMPOSITION OF DISSOLVED INORGANIC CARBON (DIC) IN PRECIPITATION FOR NORTHWESTERN ARKANSAS

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PECCI code (Python™ Estimation for Carbon Concentration and Isotopes) for Calculating the Concentration and Stable Carbon Isotopic Composition of Dissolved Inorganic Carbon (DIC) in Precipitation for northwestern Arkansas

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In karst settings, hydrograph separations using isotopic tracers are commonly and effectively used to quantify the proportions of rain rapidly delivered to springs along fractures and conduits during storm events. Dissolved inorganic carbon (DIC) is an effective, non-conservative tracer for use in hydrograph separations of karst waters because of the ubiquitous nature of carbon in the sources of waters to caves and springs and unique concentrations and isotopic compositions of carbon inputs. DIC concentration and isotopic composition (δ^{13}C-DIC) in rain are typically calculated based on atmospheric carbon dioxide (CO_2) using equilibrium carbonate reactions and stable carbon isotope fractionation values. As atmospheric CO_2 changes, traditional assumptions applied in attaining calculated values can result in error, and better estimates of rain DIC are needed. The concentration and isotopic composition of rain DIC in the karst of northwestern Arkansas was calculated using Python™ programming language based on local atmospheric CO_2 and rain pH data from 2011 to 2013. Python™ provides an open-source code and rapid means to complete iterative calculations, and the PECCI code (Python™ Estimation for Carbon Concentration and Isotopes) can be used for rain DIC calculations in other areas. Measured northwestern Arkansas atmospheric CO_2 had a median concentration of 397.7 ±4.3 ppm and increased slightly over three years and median δ^{13}C-CO_2 was -8.5 ±0.4 ‰. Rain samples exhibited a median pH of 5.6 ±0.4. Calculated rain DIC ranged from 0.17 to 0.34 mg/L and δ^{13}C-DIC ranged from -8.5‰ to -8.2‰ between 5 and 30 °C. At an average annual temperature of 14.6 °C, rain DIC was calculated to be 0.25 mg/L and δ^{13}C-DIC was -8.34 ‰. Although the variations in DIC are small, the concentration and isotopic composition of end-member sources in hydrograph separations controls the final hydrologic budget calculations. The PECCI code can be modified to calculate rain DIC for other study sites or time periods.

Introduction

Mixing models that quantify source-water contributions to karst spring flow can better constrain pollutant flux, providing a means to mitigate contamination in vulnerable karst recharge zones (Doctor et al., 2006; Trček et al., 2006). The mixing models—or hydrograph separations—when applied across a storm event use geochemical tracers (e.g., specific conductance or chloride) or isotopic tracers (e.g., δ^2H-H_2O, δ^{18}O-H_2O, or δ^{13}C-DIC) to quantify the proportion of rain delivered by various groundwater pathways to streams or springs during storm events (Lee and Krothe, 2001; Klaus and McDonnell, 2013; Knierim et al., 2013). Source-water contributions moving along quick-flow pathways convey pollutants in an unattenuated form into the subsurface and are the focus of many studies (Mahler and Garner, 2009; Lee and Krothe, 2001; Trček et al., 2006). Features such as sinkholes, losing-stream segments, and dissolution-enlarged conduits are defining elements in karst (Ford and Williams, 2007), and allow rain and surface water to rapidly enter the subsurface, thus contributing to the quick-flow component of a storm event (Lee and Krothe, 2001). Although preferential groundwater flow paths allow for rapid infiltration, pre-event water stored in the recharge zone can contribute substantial volumes (>50 %) to storm-flow discharge (Doctor et al., 2006; Lee and Krothe, 2001; Mahler and Garner, 2009; Trček et al., 2006; Knierim et al., 2013). Pre-event water may be further separated into vadose, epikarst, or phreatic water contributions in karst aquifers and includes pathways where water movement is slow relative to groundwater flow rates observed along preferential flow paths (Lee and Krothe, 2003; Knierim et al., 2013). The soil and epikarst can be important zones for biogeochemical processing of nutrients and bacteria that may otherwise enter the karst aquifer with little to no attenuation (Peterson et al., 2002; Winston, 2006; Laincz, 2014), so understanding the volume of water stored in these zones is important for developing karst hydrologic budgets.

Dissolved inorganic carbon (DIC) is a useful, non-conservative tracer for karst waters because of the ubiquitous nature of carbon in the sources of water to caves and springs (Doctor et al., 2006; Knierim et al., 2013). When non-conservative tracers are used in mixing models, the isotopic composition and concentration of the species must be accounted for because the isotopic composition reflects the solute dissolved in water, but not the water itself (Lee and Krothe, 2001). The amount of inorganically derived carbon in karst depends on pH, temperature, and the relative openness of the system for continuing input of carbon dioxide (CO_2) (Fairchild et al., 2006; Clark and Fritz, 1997). DIC concentration and isotopic composition (δ^{13}C-DIC) can be calculated for a solution with a known pH and temperature in equilibrium with a gaseous CO_2 reservoir (Clark and Fritz, 1997). DIC concentration and δ^{13}C-DIC in precipitation are typically calculated based on atmospheric CO_2 using equilibrium carbonate reactions and stable carbon isotope fractionation values (Clark and Fritz, 1997; Lee and Krothe, 2001; Das et al., 2005), although one study has directly measured DIC in rain (Górka et al., 2011).

Accurate end-member compositions are critical for generating representative hydrograph separations (Klaus and McDonnell, 2013), and rain (representative of event water or quick flow) often constitutes one of the end-member sources to storm-event flow in karst aquifers (Knierim et al., 2013; Lee and Krothe, 2001; Mahler and Garner, 2009). Atmospheric CO_2 varies over time (Forster et al., 2007) and space (Wei et al., 2014), so DIC in rainfall must also show concentration and isotopic variability. Constraining the variability of end-member sources can be one of the more difficult challenges for calculating hydrologic budgets using hydrograph separations (Kendall et al., 2001; Klaus and McDonnell, 2013); therefore, better estimates of rain DIC are needed. The

concentration and isotopic composition of rain DIC in the karst of northwestern Arkansas was calculated in Python™ programming language using the PECCI code, or Python™ Estimation of Carbon Concentration and Isotopes, based on atmospheric CO_2 and rain pH data from 2011 to 2013. Python™ provides an open-source code and rapid means to complete iterative carbonate geochemistry calculations, and the PECCI code can be used for rain DIC calculations in other areas.

Study Site

Northwestern Arkansas is situated in the Ozark Plateaus Physiographic Province (Ozarks), which is one of the major karst areas in the world (Weary and Doctor, 2014) and includes interbedded clastic and carbonate lithologies on three gently dipping plateaus (Adamski et al., 1995). Karst features such as sinkholes, caves, springs, and losing-stream segments are common in the Ozarks because of the secondary porosity developed in Paleozoic carbonate units. Northwestern Arkansas is part of the humid climate karst (Weary and Doctor, 2014) and receives an average 109 cm of precipitation annually (Adamski et al., 1995). Rainfall tends to follow a bimodal distribution, with precipitation peaking in May (13.8 cm/month) and September (10.5 cm/month) (Knierim et al., in press). Surface temperature ranged from -6.3 to 29.7 °C from January 1895 to December 2012, with a median temperature of 14.6 °C (National Oceanic Atmospheric Administration, 2013).

Methods

Data Acquisition

Atmospheric CO_2 and rain pH data were obtained from sites near northwestern Arkansas to calculate the concentration and isotopic composition of DIC in rain using equilibrium carbonate reactions and stable isotope enrichment values. CO_2 concentration and $\delta^{13}C\text{-}CO_2$ data were obtained from the National Oceanic and Atmospheric Administration's (NOAA) Earth System Research Laboratory for the Southern Great Plains, Oklahoma (SGP) site (National Oceanic Atmospheric Administration, 2014c, 2014b), which is approximately 300 km west of northwestern Arkansas. Monthly CO_2 concentration data were from 2011 to 2013 and monthly $\delta^{13}C\text{-}CO_2$ data were from 2012 to 2013. Rain chemistry data were obtained from NOAA's National Trends Network for the Fayetteville, Arkansas (AR27) site and monthly laboratory pH values were from 2011 to 2013 (National Atmospheric Deposition Program, 2014).

Carbonate Geochemistry

Equilibrium dissolved carbonate species concentrations can be calculated when gaseous CO_2, pH, and temperature are known (Clark and Fritz, 1997; Dreybrodt, 1988). DIC includes the total amount of inorganic carbon dissolved in a solution (Dreybrodt, 1988):

$$DIC = C_T = H_2CO_3^* + HCO_3^- + CO_3^{2-} \quad (1)$$

where $H_2CO_3^*$ includes dissolved CO_2 ($CO_{2(aq)}$) and carbonic acid (H_2CO_3), HCO_3^- is bicarbonate, and CO_3^{2-} is carbonate. Atmospheric CO_2 dissolves in rain to yield the $H_2CO_3^*$ species, and under equilibrium conditions $H_2CO_3^*$ is defined by the equation:

$$H_2CO_3^* = 10^{-pK_{CO_2}} \times pCO_2 \quad (2)$$

where pK_{CO2} is a temperature-dependent equilibrium constant (Table 1) (Plummer and Busenberg, 1982) and pCO_2 is the partial pressure of gaseous CO_2 in atmospheres. $H_2CO_3^*$ disassociates in water to form HCO_3^-, and under equilibrium conditions HCO_3^- is defined by the equation:

$$HCO_3^- = \frac{10^{-pK_1} \times H_2CO_3^*}{H^+} \quad (3)$$

where pK_1 is a temperature-dependent equilibrium constant (Table 1) (Plummer and Busenberg, 1982) and $H+$ is the concentration of hydrogen ions in solution, as defined by pH.

HCO_3^- disassociates in water to form CO_3^{2-}, and under equilibrium conditions CO_3^{2-} is defined by the equation:

$$CO_3^{2-} = \frac{10^{-pK_2} \times HCO_3^-}{H^+} \quad 4$$

where pK_2 is a temperature-dependent equilibrium constant (Table 1) (Plummer and Busenberg, 1982). In Equations 2 through 4, chemical activity was assumed to equal the concentration of a species because the activity coefficient approaches 1 for very dilute solutions (Dreybrodt, 1988), such as precipitation. Equations 1 through 4 were encoded using Python™ and used to calculate the concentration of DIC in rain and the proportion of carbonate species, as controlled by pH.

Isotopic fractionation occurs for each carbonate speciation step when CO_2 dissolves in water, hydrates into $H_2CO_3^*$, and dissociates into HCO_3^- and CO_3^{2-}; each resultant carbonate species has an empirically derived, temperature-dependent enrichment factor, or ε (Table 1) (Clark and Fritz, 1997). For each carbonate species pair, where a carbon-isotope exchange is possible, ε describes the difference in isotopic compositions between species, and a gross enrichment factor can be used to sum the total result of these exchanges. The gross fractionation between aqueous DIC and gaseous CO_2 ($\varepsilon^{13}C_{DIC\text{-}CO_{2(g)}}$) is dependent on the proportion of carbonate species in solution and defined by the following equation (Clark and Fritz, 1997; Peyraube et al., 2013):

$$\varepsilon^{13}C_{DIC-CO_{2(g)}} = \left(\varepsilon^{13}C_{CO_{2(aq)}-CO_2} \times {H_2CO_3^*}/{DIC}\right) + \left(\varepsilon^{13}C_{HCO_3-CO_2} \times {HCO_3^-}/{DIC}\right) + \left(\varepsilon^{13}C_{H_2CO_3-CO_2} \times {CO_3^{2-}}/{DIC}\right) \quad 5$$

Equation 5 was encoded using Python™ and applied to calculate the isotopic composition of DIC in rain, as controlled by the proportion of carbonate species calculated using Equations 2 through 4.

Data Analysis

The concentration of DIC in rain was calculated using Equations 1 through 4, incorporating pH of rain from AR27, atmospheric CO_2 concentration from SGP, and temperature-dependent carbonate equilibrium constants (Table 1). Median values for CO_2 concentration and rain pH were used in the calculations. The δ^{13}C-DIC in rain was calculated using Equation 5, incorporating the isotopic composition of atmospheric CO_2 from SGP, and temperature-

Table 1. Carbonate equilibrium constants and stable carbon isotope enrichment values.

Temperature (°C)*	pK_{CO2}	pK_1	pK_2	pK_{sp}	Temperature (°C)**	$\varepsilon^{13}C_{CO2(aq)\text{-}CO2(g)}$	$\varepsilon^{13}C_{HCO3\text{-}CO2(g)}$	$\varepsilon^{13}C_{CO3\text{-}CO2(g)}$
0	1.11	6.58	10.63	8.38	0	-1.2	10.9	11.4
5	1.19	6.52	10.55	8.39	5	-1.2	10.2	9.8
10	1.27	6.46	10.49	8.41	10	-1.1	9.6	9.2
15	1.34	6.42	10.43	8.43	15	-1.1	9.0	8.6
20	1.41	6.38	10.38	8.45	20	-1.1	8.5	8.1
25	1.47	6.35	10.33	8.48	25	-1.1	7.9	7.6
30	1.52	6.33	10.29	8.51	35	-1.0	6.9	6.6
45	1.67	6.29	10.20	8.62	50	-1.0	5.5	5.2
60	1.78	6.29	10.14	8.76	75	-0.9	3.3	3.2

* Carbonate equilibrium constants from (Plummer and Busenberg 1982)
**Carbon isotope enrichment values from (Clark and Fritz 1997)

dependent isotopic enrichment values (Table 1). The median $\delta^{13}C$-CO_2 value was used in the calculations. Calculations were completed in five-degree temperature increments from 5 to 30 °C based on the range of temperatures observed in northwestern Arkansas (National Oceanic Atmospheric Administration, 2013). The PECCI code can be found in the Appendix.

Results and Discussion

Atmospheric CO_2

Atmospheric CO_2 in northeastern Oklahoma ranged from 386.9 to 404.6 ppm (Table 2) with a median concentration of 397.7 ±4.3 ppm between January 2011 and December 2013 (Fig. 1), exhibiting a slight increase and over time (Fig. 2). Atmospheric $\delta^{13}C$-CO_2 ranged from -10.0‰ to -8.2‰ (Table 3) with a median value of -8.5 ±0.4 ‰ between January 2011 and December 2012 (Fig. 3). Globally, the concentration of atmospheric CO_2 is increasing and $\delta^{13}C$-CO_2 values are decreasing over time due to anthropogenic fossil fuel combustion and land-use changes (Forster et al., 2007). These global relations can be observed in the CO_2 data from SGP; CO_2 increased by 4 ppm over three years (Fig. 2) and $\delta^{13}C$-CO_2 decreased by 1 ‰ over two years (Fig. 4). In the absence of direct measurements of alkalinity or DIC, atmospheric CO_2 concentration is required to calculate DIC in rain (Eqn. 2), so changes in atmospheric CO_2 concentration over time (Forster et al., 2007) and space (Wei et al., 2014) need to be taken into account. Additionally, when using DIC as an isotopic tracer, local $\delta^{13}C$-CO_2 values should be used because atmospheric CO_2 isotopic compositions also vary globally (National Oceanic Atmospheric Administration, 2014a). Direct measurement of DIC in precipitation has shown that atmospheric CO_2 and DIC in precipitation may not always be in equilibrium (Górka et al., 2011), but constraining local variations in CO_2 concentration and isotopic composition should provide a better estimate of rain DIC than using global values.

Table 2. Atmospheric CO_2 concentration from Southern Great Plains, Oklahoma (SGP).

Date	CO_2 (ppm)	Date	CO_2 (ppm)
Jan. 2011	400.75	Jul. 2012	394.22
Feb. 2011	400.21	Aug. 2012	393.91
Mar. 2011	399.46	Sep. 2012	396.54
Apr. 2011	398.64	Oct. 2012	398.83
May. 2011	394.33	Nov. 2012	400.50
Jun. 2011	391.01	Dec. 2012	403.37
Jul. 2011	395.48	Jan. 2013	404.15
Aug. 2011	394.19	Feb. 2013	404.62
Sep. 2011	386.87	Mar. 2013	403.94
Oct. 2011	389.81	Apr. 2013	400.52
Nov. 2011	396.72	May. 2013	399.04
Dec. 2011	397.84	Jun. 2013	397.63
Jan. 2012	398.13	Jul. 2013	394.69
Feb. 2012	398.95	Aug. 2013	392.45
Mar. 2012	395.29	Sep. 2013	394.31
Apr. 2012	391.67	Oct. 2013	398.51
May. 2012	394.10	Nov. 2013	402.08
Jun. 2012	396.10	Dec. 2013	404.57

Note: Data from National Oceanic Atmospheric Administration (2014a)

Table 3. Atmospheric CO_2 isotopic composition from Southern Great Plains, Oklahoma (SGP).

Date	$\delta^{13}C$-CO_2 (‰)	Date	$\delta^{13}C$-CO_2 (‰)
Jan. 2011	-8.81	Jan. 2012	-8.63
Feb. 2011	-8.81	Feb. 2012	-8.56
Mar. 2011	-8.76	Mar. 2012	-8.44
Apr. 2011	-8.63	Apr. 2012	-8.32
May. 2011	-8.59	May. 2012	-8.38
Jun. 2011	-8.51	Jun. 2012	-8.48
Jul. 2011	-8.33	Jul. 2012	-8.40
Aug. 2011	-8.20	Aug. 2012	-8.29
Sep. 2011	-8.19	Sep. 2012	-8.32
Oct. 2011	-8.26	Oct. 2012	-8.66
Nov. 2011	-8.49	Nov. 2012	-9.37
Dec. 2011	-8.65	Dec. 2012	-9.96

Note: Data from National Oceanic Atmospheric Administration (2014b)

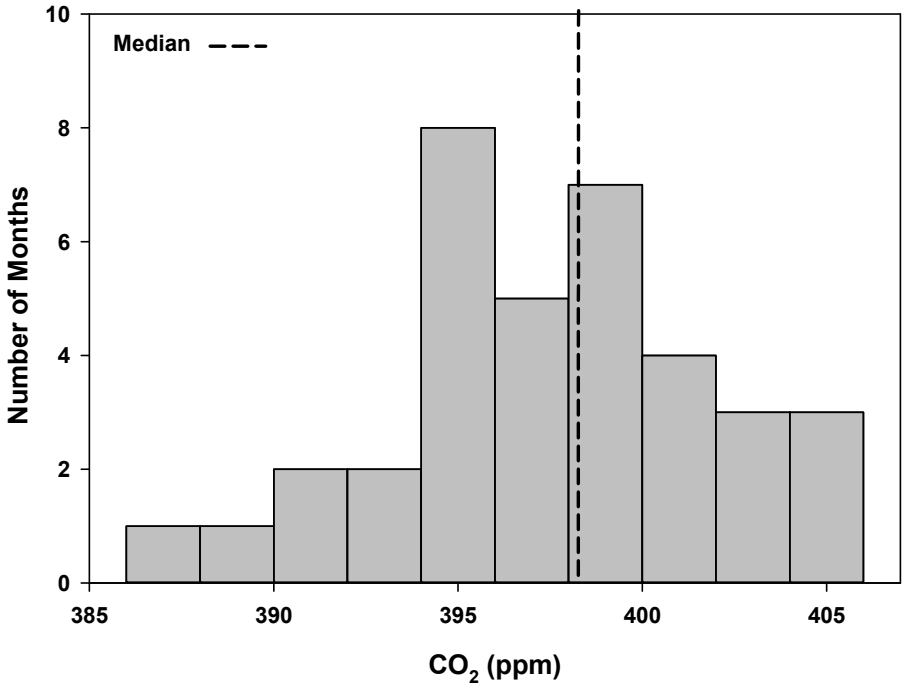

Figure 1. Histogram of atmospheric CO_2 concentration at Southern Great Plains, Oklahoma from 2011 to 2012.

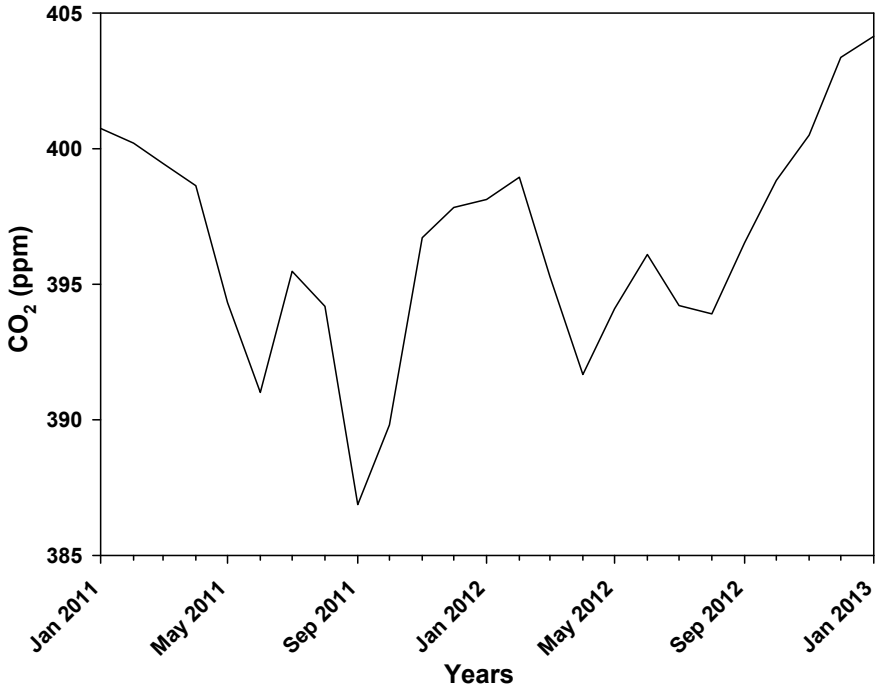

Figure 2. Atmospheric CO_2 concentration at Southern Great Plains, Oklahoma over time.

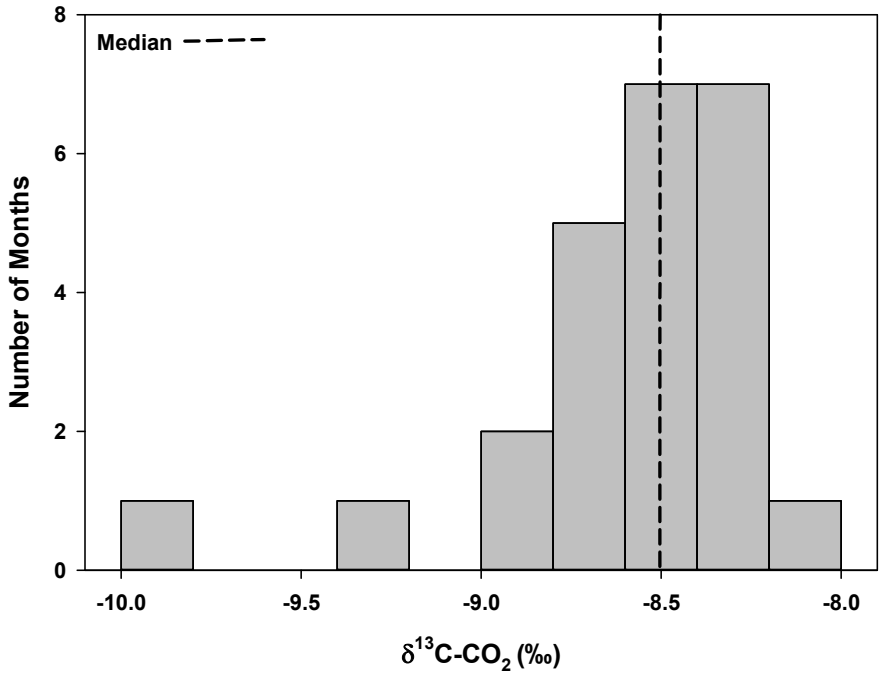

Figure 3. Histogram of atmospheric CO_2 isotopic composition at Southern Great Plains, Oklahoma from 2012 to 2013.

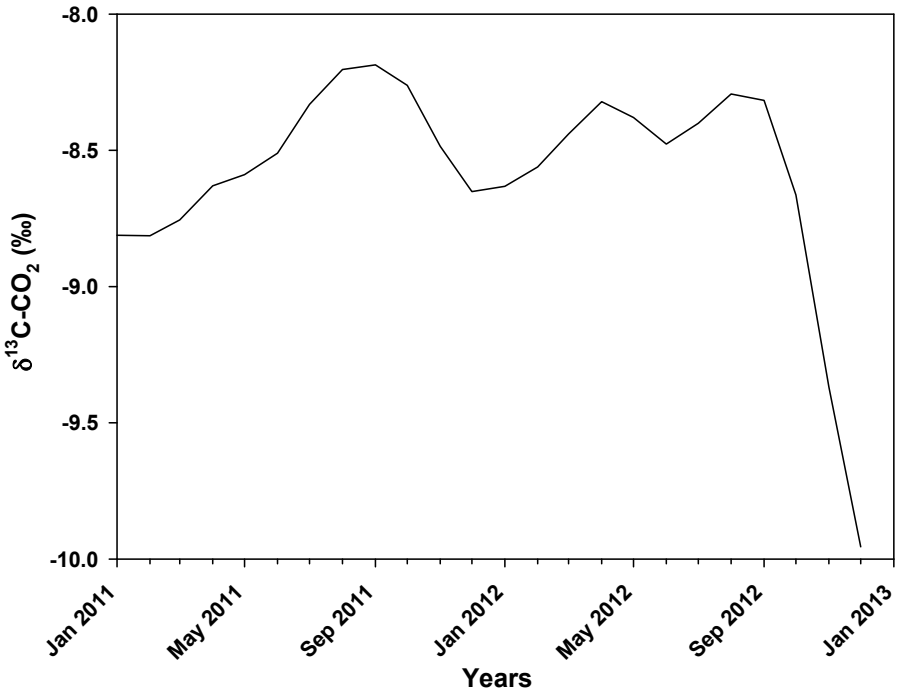

Figure 4. Atmospheric CO_2 isotopic composition at Southern Great Plains, Oklahoma over time.

Rain pH

Laboratory pH values from rain samples ranged from 4.9 to 6.4 (Table 4) and had a median value of 5.6 ± 0.4 between 2011 and 2013 (Fig. 5). pH values varied among storm events, but did not show a trend through time (Fig. 6). The pH values for precipitation from northwestern Arkansas were slightly acidic because of the exchange of atmospheric CO_2, NO_X, and SO_2 with falling rain drops. Most of the measured precipitation pH values at AR27 were below 6.4 (Fig. 5), and for pH values up to 6.4, DIC will be dominated by $H_2CO_3^*$ (Clark and Fritz, 1997). The isotopic enrichment factors are much larger between HCO_3^- or CO_3^{2-} and gaseous CO_2 compared to $H_2CO_3^*$ and gaseous CO_2 (Table 1); therefore, even small proportions of HCO_3^- in precipitation (as controlled by pH) need to be accounted for to properly weight the gross isotopic enrichment between DIC and CO_2. For example, if CO_2 concentration is 400 ppm and $\delta^{13}C\text{-}CO_2$ is -8.0 ‰, at rain pH of 6.0, $\varepsilon^{13}C_{DIC\text{-}CO2}$ will be 1.7 ‰ at 25 °C, which results in $\delta^{13}C$-DIC of -6.3 ‰. If CO_2 concentration and isotopic composition are held constant, at rain pH of 4.5, $\varepsilon^{13}C_{DIC\text{-}CO2}$ will be -1.0 ‰, which results in $\delta^{13}C$-DIC of -9.0 ‰. Rain DIC isotopic composition can vary significantly from pH values of 4 to 7, because of the change in fractionation between gaseous CO_2 and $H_2CO_3^*$ to HCO_3 at the critical pH value of 6.4 (Clark and Fritz, 1997). Additionally, an end-member rain DIC composition that varies by 2.7 ‰, such as in this example, will affect subsequent mixing model calculations and the final hydrograph separation.

Table 4. Rain pH data from Fayetteville, Arkansas (AR27).

Date	pH	Date	pH
Jan. 2011	6.05	Jul. 2012	6.22
Feb. 2011	6.44	Aug. 2012	--
Mar. 2011	5.79	Sep. 2012	5.78
Apr. 2011	6.02	Oct. 2012	--
May. 2011	5.99	Nov. 2012	--
Jun. 2011	4.92	Dec. 2012	--
Jul. 2011	5.14	Jan. 2013	6.00
Aug. 2011	5.06	Feb. 2013	5.50
Sep. 2011	5.10	Mar. 2013	5.84
Oct. 2011	5.12	Apr. 2013	5.87
Nov. 2011	5.36	May. 2013	5.71
Dec. 2011	5.23	Jun. 2013	5.67
Jan. 2012	5.51	Jul. 2013	5.43
Feb. 2012	5.40	Aug. 2013	5.50
Mar. 2012	5.92	Sep. 2013	5.15
Apr. 2012	5.73	Oct. 2013	5.59
May. 2012	6.36	Nov. 2013	5.32
Jun. 2012	5.57	Dec. 2013	5.30

'--' means data not available
Note: Data from National Atmospheric Deposition Program (2014)

DIC in Rain

Carbonate equilibrium constants are temperature dependent, so the concentration of DIC between 5 and 30°C varied following the equation:

$$DIC = 1.43 \times 10^{-4}T^2 - 1.19 \times 10^{-2}T + 3.97 \times 10^{-1} \quad 6$$

where T is temperature in °C, and DIC was converted to mg/L using molar weights. Calculated DIC in rain for northwestern Arkansas ranged from 0.17 to 0.34 mg/L between 5 and 30°C (Fig. 7). The proportions of carbonate species in DIC is controlled by pH and temperature (Clark and Fritz, 1997) and, for example, at a median value of 5.6 and 25°C, $H_2CO_3^*$ constituted 86% of DIC.

Isotopic enrichment between DIC and atmospheric CO_2 also varied with temperature and was defined by the equation:

$$\varepsilon^{13}C_{DIC-CO_{2(g)}} = -3.86 \times 10^{-4}T^2 + 2.36 \times 10^{-2}T - 1.04 \times 10^{-1} \quad 7$$

$\varepsilon^{13}C_{DIC-CO_{2(g)}}$ ranged from 0.0 (no fractionation) to 0.3 ‰ between 5 and 30 °C (Fig. 8).

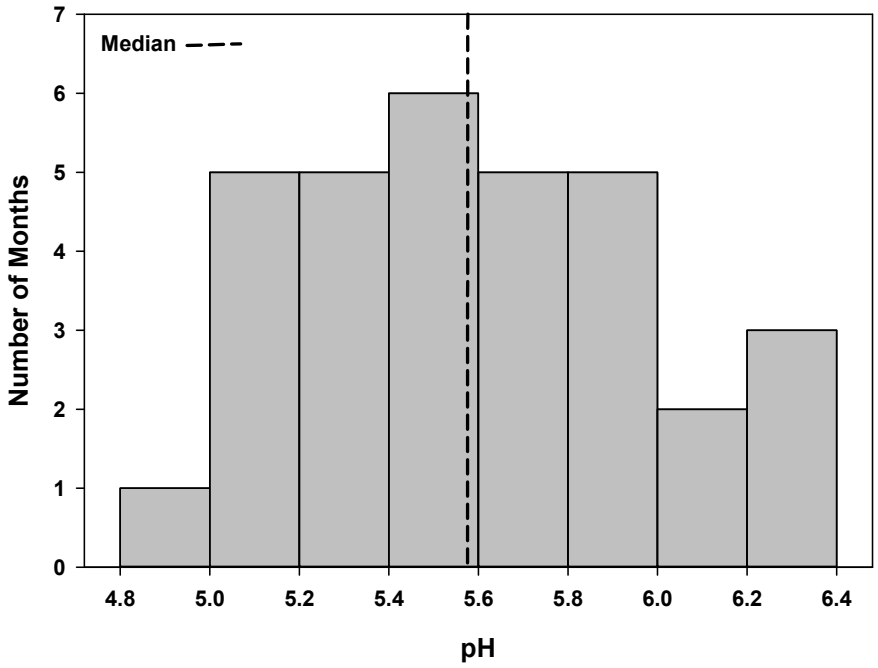

Figure 5. Histogram of rain pH at Fayetteville, Arkansas.

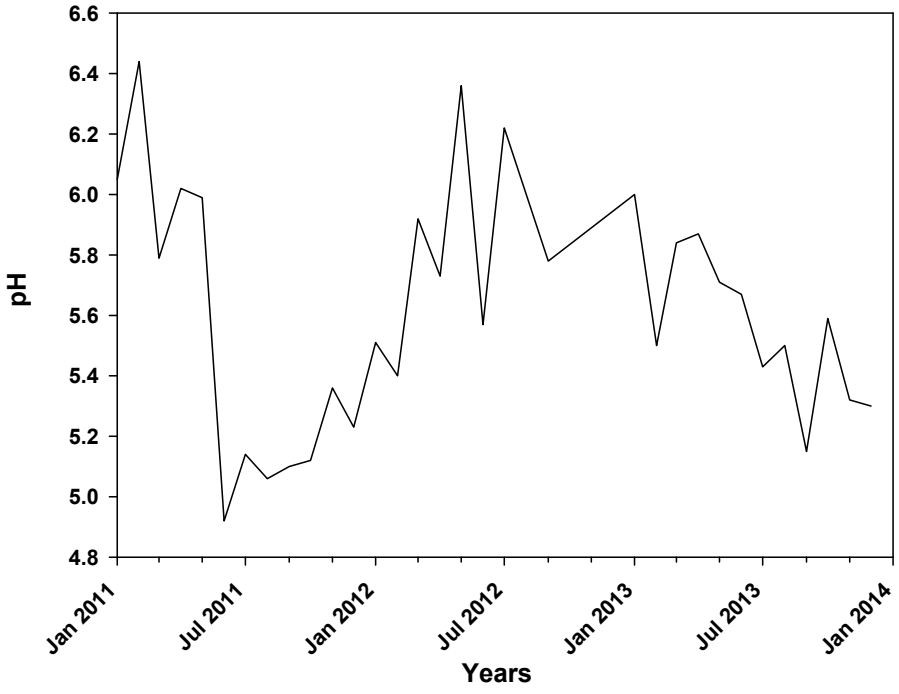

Figure 6. Rain pH at Fayetteville, Arkansas over time.

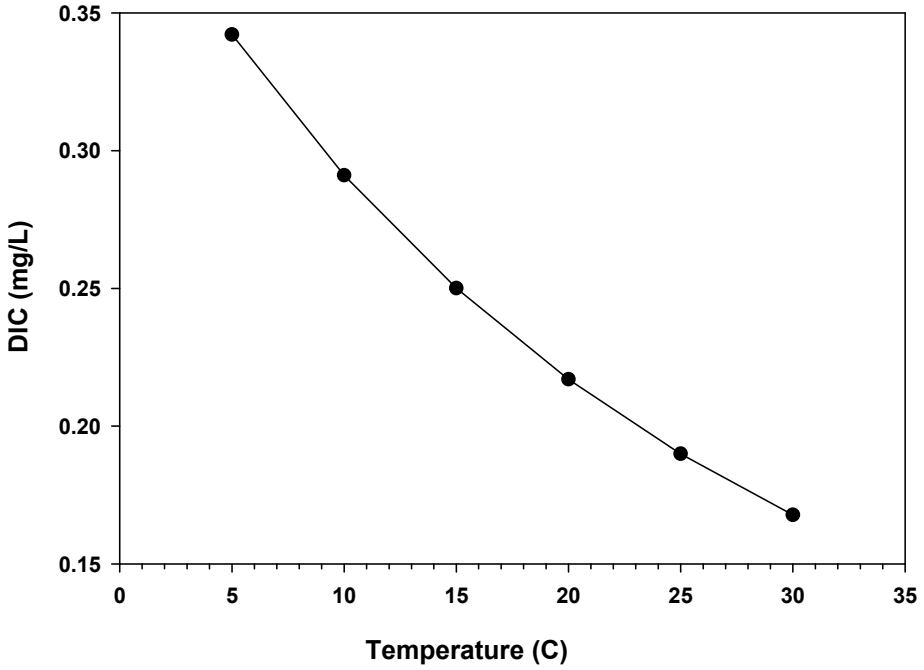

Figure 7. DIC concentration in rain for northwestern Arkansas.

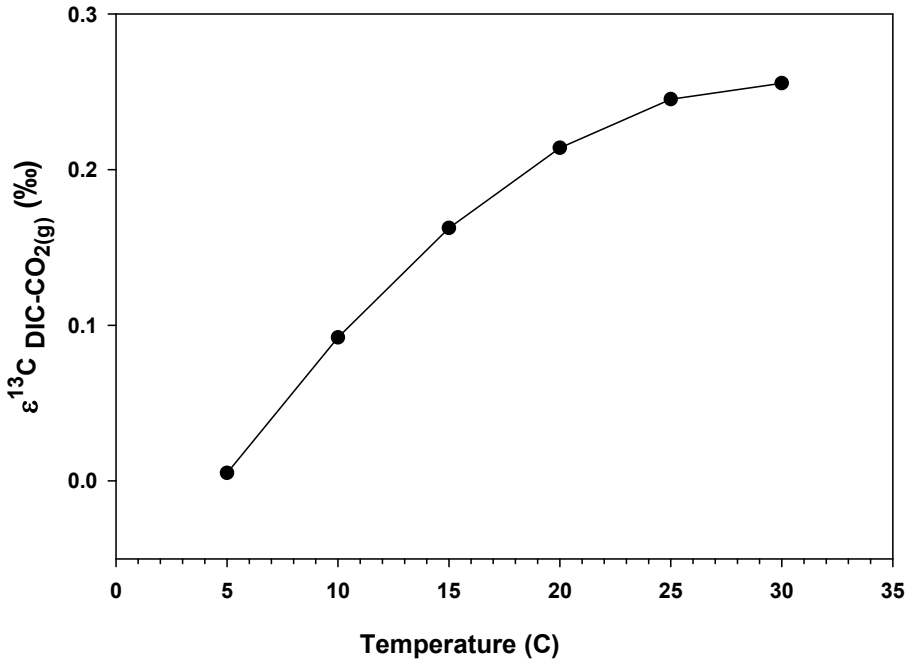

Figure 8. Isotopic enrichment between DIC in rain and atmospheric CO_2 for northwestern Arkansas.

Fractionations between dissolved carbonate species and gaseous CO_2 were weighted based on the proportion of each species in DIC, following Equation 5 (Clark and Fritz, 1997; Peyraube et al., 2013). The weighted, gross fractionation provided a more accurate estimate of δ^{13}C-DIC, because if all the DIC was assumed to be $H_2CO_3^*$, then the enrichment would be closer to 1 ‰ (Lee and Krothe, 2001).

Using $\varepsilon^{13}C_{DIC-CO_{2(g)}}$ (Fig. 8) and the median value of δ^{13}C-CO_2 at SGP (Fig. 3), the theoretical isotopic composition of DIC in rain was defined by the equation:

$$\delta^{13}C - DIC = -3.86 \times 10^{-4}T^2 + 2.36 \times 10^{-2}T - 8.60 \quad 8$$

The isotopic composition of DIC ranged from -8.5‰ to -8.2‰ between 5 and 30 °C (Fig. 9). Based on global trends in atmospheric CO_2 (Forster et al., 2007), DIC concentration is predicted to increase and δ^{13}C-DIC will become lighter, if temperature and pH are held constant. But, because of the nature of the carbon cycle through the atmosphere, hydrosphere, and geosphere, rain pH and temperature will also likely change in the future. Therefore, geochemical and isotopic balances of rain DIC will need to account for the changing variables of temperature, pH, and CO_2.

Perhaps the most difficult aspect to constrain when calculating DIC concentration and isotopic composition in rain is temperature because (1) equilibrium carbonate constants and carbon isotope enrichment factors are temperature dependent and (2) temperature varies greatly in the temperate mid-latitudes, such as north-western Arkansas. Additionally, what is the temperature of precipitation and does that temperature have any relation with surface air temperature? Air temperature depends on the environmental lapse rate and varies with altitude (Aguado and Burt, 2004). Condensation in the atmosphere in the mid-latitudes forms as ice crystals, so the type of precipitation that falls to the ground is controlled by surface air temperature (Aguado and Burt, 2004), but the relation between surface temperature and precipitation temperature is controlled by a complex set of thermodynamic relations not fully explored here. In an urban precipitation study, rain DIC formed in ambient air temperatures, but not in equilibrium with atmospheric CO_2 (Górka et al., 2011). Therefore, completing the DIC calculations over the range of temperatures observed at a specific study site provides a means to quantify how temperature controls DIC concentration and δ^{13}C-DIC of rain.

From 5 to 30°C, calculated DIC concentration varied by 0.2 mg/L and δ^{13}C-DIC by 0.3 ‰. Based on the small variation in DIC over the range of temperatures observed in northwestern Arkansas, and using the median temperature of 14.6 °C, rain DIC was calculated to be 0.25 mg/L and δ^{13}C-DIC was -8.34 ‰. Although these variations are small, the concentration and isotopic composition of end-member sources in hydrograph separations controls the final hydrologic budget calculations (Doctor et al., 2006; Lee and Krothe, 2001). Additionally, rain DIC was calculated for a single atmospheric CO_2 concentration, δ^{13}C-CO_2 composition, and rain pH value for data sets over two to three years. The PECCI code can be modified to calculate DIC concentration and isotopic composition for rain events on a weekly basis (based on the available CO_2 data), allowing more detailed calculations over time. The PECCI code can also be modified to calculate rain DIC for other study sites.

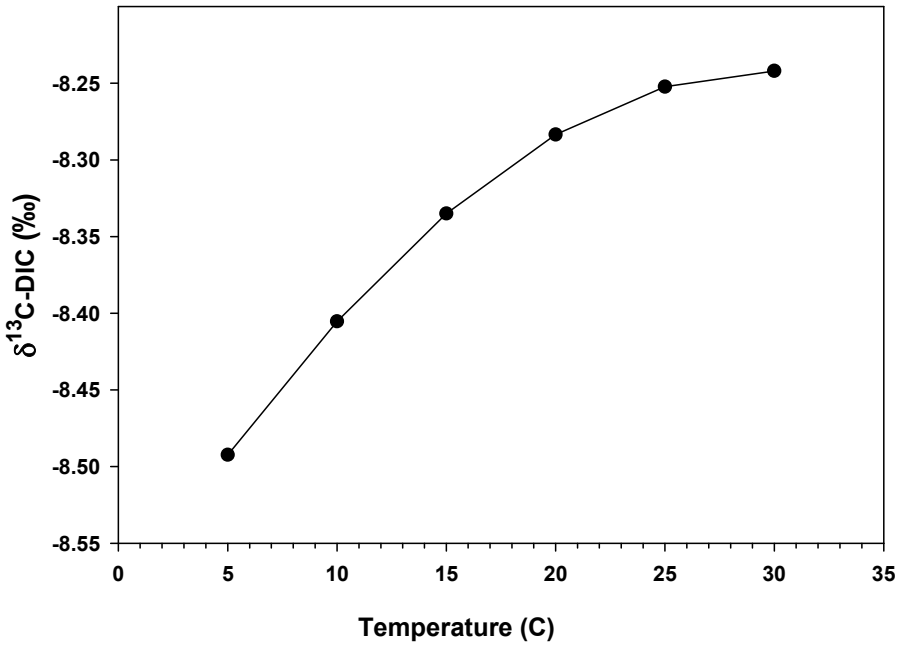

Figure 9. Isotopic composition of rain DIC for northwestern Arkansas.

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Appendix. The PECCI code calculates the DIC concentration and δ^{13}C-DIC composition of precipitation using atmospheric CO_2 concentration, atmospheric δ^{13}C-CO_2 composition, and rain pH data. This code can be used in Python™ programming language. Notes for users are designated by a pound sign, "#", and bold font.

```
#This loads the necessary functions for Python
from scipy.stats import linregress
from scipy.stats import pearsonr
from scipy.stats import ttest_ind
from scipy.stats.distributions import t
import numpy as np
from pandas import *
import pandas as pd

#First, the constants for carbonate equilibrium reactions (Fetter, 2001) and stable carbon isotope
#equilibrium enrichment values (Clark and Fritz, 1997) are defined
#See Table 1 for the carbonate equilibria used in this program
#Convert Table 1 to a text file to load into the program or use relevant thermodynamic equations
c_constants = loadtxt('Rain_Code/CarbonConstants.csv',skiprows=2, delimiter=',')
temp_c = c_constants[:,0]
pKCO2 = c_constants[:,1]
pK1 = c_constants[:,2]
pK2 = c_constants[:,3]
temp_e = c_constants[:,5]
eH2CO3 = c_constants[:,6]
eHCO3 = c_constants[:,7]
eCO3 = c_constants[:,8]
print c_constants
#This is the input file with Temperature, KCO2, K1, K2, and KSP(calcite) from Fetter (2001) and
#Temperature, eH2CO3, eHCO3, eCO3 from Clark and Fritz (1997)

#Next, the regressions for carbonate equilibria are calculated relative to temperature in degrees
#Celsius.
#Equations and plot for KCO2
coeff_KCO2 = polyfit(temp_c, pKCO2, 2)
model_KCO2 = poly1d(coeff_KCO2)
model_KCO2(temp_c)
xlim([-10,70])
ylim([1.0,1.8])
plot(temp_c, pKCO2, 'ko')
plot(temp_c, model_KCO2(temp_c), 'k')
xlabel(r'Temperature ($\degree$C)',fontsize=14)
ylabel(r'pK$_{CO2}$', fontsize=14)
print "Coefficients for pKCO2 equation", coeff_KCO2
savefig("pKCO2_constant.png")
KCO2_a = coeff_KCO2[0]
```

```
KCO2_b = coeff_KCO2[1]
KCO2_c = coeff_KCO2[2]

#Equations and plot for K1
coeff_K1 = polyfit(temp_c, pK1, 2)
model_K1 = poly1d(coeff_K1)
model_K1(temp_c)
plot(temp_c, pK1, 'ko')
plot(temp_c, model_K1(temp_c),'k')
xlim([-10,70])
xlabel(r'Temperature ($\degree$C)',fontsize=14)
ylabel('pK$_{1}$', fontsize=14)
print "Coefficients for pK1 equation", coeff_K1
savefig("pK1_constant.png")

K1_a = coeff_K1[0]
K1_b = coeff_K1[1]
K1_c = coeff_K1[2]

#Equations and plot for K2
coeff_K2 = polyfit(temp_c, pK2, 2)
model_K2 = poly1d(coeff_K2)
model_K2(temp_c)
plot(temp_c, pK2, 'ko')
plot(temp_c, model_K2(temp_c),'k')
xlim([-10,70])
xlabel(r'Temperature ($\degree$C)',fontsize=14)
ylabel('pK$_{2}$', fontsize=14)
print "Coefficients for pK2 equation", coeff_K2
savefig("pK2_constant.png")

K2_a = coeff_K2[0]
K2_b = coeff_K2[1]
K2_c = coeff_K2[2]

#Equations and plot for eH2CO3 (enrichment value for H2CO3-CO2(gas))
slope_H2CO3, intercept_H2CO3, r_H2CO3, p_H2CO3, stderr_H2CO3 = linregress(temp_e, e++++H2CO3)
y_lin_H2CO3 = slope_H2CO3*temp_e+intercept_H2CO3
plot(temp_e,y_lin_H2CO3, 'k')
plot(temp_e, eH2CO3, 'ko')
ylim([-1.25, -0.85])
xlim([-10,80])
xlabel(r'Temperature ($\degree$C)',fontsize=14)
ylabel(ur'$\epsilon^{13}C_{CO_2(aq)-CO_2(g)} (\u2030)$', fontsize=15)
print 'Slope =', slope_H2CO3
print 'Intercept =', intercept_H2CO3
print 'R^2 =', r_H2CO3**2.
```

```
print 'p =', p_H2CO3
print 'stderr =', stderr_H2CO3
savefig("eH2CO3.png")

#Equations and plot for eHCO3 (enrichment value for HCO3-CO2(gas))
slope_HCO3, intercept_HCO3, r_HCO3, p_HCO3, stderr_HCO3 = linregress(temp_e, eHCO3)
y_lin_HCO3 = slope_HCO3*temp_e+intercept_HCO3
plot(temp_e,y_lin_HCO3,'k')
plot(temp_e, eHCO3, 'ko')
ylim([2,12])
xlim([-10,80])
xlabel(r'Temperature ($\degree$C)',fontsize=14)
ylabel(ur'$\epsilon^{13}C_{HCO_3-CO_2(g)} (\u2030)$', fontsize=15)
print 'Slope =', slope_HCO3
print 'Intercept =', intercept_HCO3
print 'R^2 =', r_HCO3**2.
print 'p =', p_HCO3
print 'stderr =', stderr_HCO3
tight_layout()
savefig("eHCO3.png")

#Equations and plot for eCO3 (enrichment value for CO3-CO2(gas))
slope_CO3, intercept_CO3, r_CO3, p_CO3, stderr_CO3 = linregress(temp_e, eCO3)
y_lin_CO3 = slope_CO3*temp_e+intercept_CO3
plot(temp_e,y_lin_CO3,'k')
plot(temp_e, eCO3, 'ko')
xlim([-10,80])
xlabel(r'Temperature ($\degree$C)',fontsize=14)
ylabel(ur'$\epsilon^{13}C_{CO_3-CO_2(g)} (\u2030)$', fontsize=15)
print 'Slope =', slope_CO3
print 'Intercept =', intercept_CO3
print 'R^2 =', r_CO3**2.
print 'p =', p_CO3
print 'stderr =', stderr_CO3
tight_layout()
savefig("eCO3.png")

#Next, load d13C-CO2 isotopic data.  These data are from NOAA's Earth Systems Research Laboratory
#at: http://www.esrl.noaa.gov/gmd/dv/data/?site=SGP&parameter_name=C13%252FC12%2Bin%2B
#Carbon%2BDioxide
#Data are from 2011 to 2012
#For an example, see Table 3
#Convert Table 3 to a text file, or load your own data into the program
SGP_13CO2 = loadtxt('Rain_Code/SGP_CO2_isodata.txt',skiprows=1, dtype='str')
SGP_13CO2_data = array(SGP_13CO2[:,3], dtype = 'float')
print SGP_13CO2_data
```

```
#Calculate the mean, median, and range of values for the data.
#The median isotopic composition (SGP_13CO2_med) is what will be used in subsequent calculations
SGP_13CO2_mean = SGP_13CO2_data.mean()
SGP_13CO2_std = SGP_13CO2_data.std(ddof=1)
SGP_13CO2_med = median(SGP_13CO2_data)
SGP_13CO2_min = min(SGP_13CO2_data)
SGP_13CO2_max = max(SGP_13CO2_data)
print 'SGP 13C-CO2 mean = ', SGP_13CO2_mean
print 'SGP 13C-CO2 median = ', SGP_13CO2_med
print 'SGP 13C-CO2 standard deviation = ', SGP_13CO2_std
print 'SGP 13C-CO2 minimum =', SGP_13CO2_min
print 'SGP 13C-CO2 maximum =', SGP_13CO2_max

#This creates a histogram of the d13C-CO2 data
hist(SGP_13CO2_data, bins=10, facecolor='w')
xplot_med_SGP13CO2 = array([SGP_13CO2_med,SGP_13CO2_med])
yplot_13CO2 = array([0,10])
plot(xplot_med_SGP13CO2, yplot_13CO2, 'k--')
legend(['Median'], 'upper left', frameon=False)
xlabel(ur'$\delta^{13}C-CO_2 (\u2030)$', fontsize = 16)
ylabel('Number of months', fontsize = 14)
tight_layout()
savefig("SGP_13CCO2_hist.png")
iso_CO2_SGP = read_csv('Rain_Code\SGP_CO2_isodata.txt',
   delim_whitespace=True,
   index_col=0,
   parse_dates=[[1,2]])
iso_CO2_SGP_data = iso_CO2_SGP["d13C_CO2"]
iso_CO2_SGP_data.plot(style='k')
xlabel("Years", fontsize=13)
ylabel(ur'$\delta^{13}C-CO_2 (\u2030)$', fontsize=16)
tight_layout()
savefig("SGP_13CCO2_time.png")

#Next, load CO2 concentration data. These data are from NOAA's Earth Systems Research Laboratory
#at: http://www.esrl.noaa.gov/gmd/dv/data/?parameter_name=Carbon%2BDioxide&site=SGP
#Data are from 2011 to 2013
#For an example, see Table 2
#Convert Table 2 to a text file, or load your own data into the program
SGP_CO2 = loadtxt('Rain_Code\SGP_CO2_concdata.txt', skiprows=1, dtype='str')
SGP_CO2_data = array(SGP_CO2[:,3], dtype = 'float')
print SGP_CO2_data

#Calculate the mean, median, and range of values for the data. The median concentration
(SGP_CO2_med) is what will be used in subsequent calculations
SGP_CO2_mean = SGP_CO2_data.mean()
SGP_CO2_std = SGP_CO2_data.std(ddof=1)
```

```
SGP_CO2_med = median(SGP_CO2_data)
SGP_CO2_min = min(SGP_CO2_data)
SGP_CO2_max = max(SGP_CO2_data)
print 'SGP CO2 mean = ', SGP_CO2_mean
print 'SGP CO2 median = ', SGP_CO2_med
print 'SGP CO2 standard deviation = ', SGP_CO2_std
print 'SGP CO2 minimum =', SGP_CO2_min
print 'SGP CO2 maximum =', SGP_CO2_max

#This creates a histogram of the CO2 data
hist(SGP_CO2_data, bins=10, facecolor='w')
xplot_med_SGPCO2 = array([SGP_CO2_med,SGP_CO2_med])
xplot_mean_SGPCO2 = array([SGP_CO2_mean,SGP_CO2_mean])
yplot_CO2 = array([0,10])
plot(xplot_med_SGPCO2, yplot_CO2, 'k--')
legend(['Median'], 'upper left', frameon=False)
xlabel(r'CO$_2$ (ppm)', fontsize = 15)
ylabel("Number of months", fontsize = 14)
savefig("SGP_CO2_hist.png")
CO2_SGP = read_csv('Rain_Code\SGP_CO2_concdata.txt',
   delim_whitespace=True,
   index_col=0,
   parse_dates=[[1,2]])
CO2_SGP_data = CO2_SGP["CO2"]
CO2_SGP_data.plot(style='k')
xlabel("Years", fontsize=13)
ylabel(r"CO$_2$ (ppm)", fontsize=13)
savefig("SGP_CO2_time.png")

#To convert between CO2 in ppm and CO2 in atm (assuming the total atmospheric volume is 1 atm):
#Note that this is the CO2 concentration used for calculating the concentration of DIC in rain.
CO2_med_atm = SGP_CO2_med*10**-6
print 'Median CO2 Concentration (atm):', CO2_med_atm

#Next, load the rain pH data.  These data are from the NOAA National Atmospheric Deposition
#Program's NTN data set
#For an example, see Table 4
#Convert Table 4 to a text file, or load your own data into the program
AR27_pH = loadtxt('Rain_Code/AR27_pHdata.txt',skiprows=1, dtype='str')
AR27_pH_data = array(AR27_pH[:,3], dtype = 'float')
print AR27_pH_data

#Calculate the mean, median, and range of pH data
AR27_pH_mean = AR27_pH_data.mean()
AR27_pH_std = AR27_pH_data.std(ddof=1)
AR27_pH_med = median(AR27_pH_data)
AR27_pH_min = min(AR27_pH_data)
```

```
AR27_pH_max = max(AR27_pH_data)
print "Mean of Monthly Lab pH", AR27_pH_mean
print "Median of Monthly Lab pH", AR27_pH_med
print "Standard Deviation of Monthly Lab pH", AR27_pH_std
print "Minimum of Monthly Lab pH", AR27_pH_min
print "Maximum of Monthly Lab pH", AR27_pH_max

#This creates a histogram of the pH data
hist(AR27_pH_data, bins=10, facecolor='w')
xlabel("pH", fontsize = 14)
xplot_med_pH = array([AR27_pH_med,AR27_pH_med])
yplot_pH = array([0,6])
plot(xplot_med_pH, yplot_pH, 'k--')
ylabel("Number of months", fontsize=14)
legend(['Median'], 'upper right', frameon=False)
savefig("AR27_pH_hist.png")
AR27_pH = read_csv('Rain_Code\AR27_pHdata.txt',
   delim_whitespace=True,
   index_col=0,
   parse_dates=[[1,2]])
AR27_pH_data = AR27_pH["pH"]
AR27_pH_data.plot(style='k')
xlabel("Years", fontsize=13)
ylabel("pH", fontsize=13)
savefig("AR27_pH_time.png")

#To convert pH to concentration of hydrogren ions:
#Note that this is the hydrogen ion concentration used to calculate the proportion of carbon species in
#DIC.
H = 10**(-1*AR27_pH_med)
print 'Hydrogen Ion Concentration of Rain:', H

#Next, build the variables for the carbonate equilibrium reactions.  This code starts at 5 degrees
#Celsius and continues in 5 degree increments to 30 degrees Celsius.

#Code for carbonate equilibria at 5 degrees Celsius:
pKCO2_5 = KCO2_a*5**2 + KCO2_b*5+KCO2_c
pK1_5 = K1_a*5**2 + K1_b*5+K1_c
pK2_5 = K1_a*5**2 + K2_b*5+K2_c
print "pKCO2 at 5 degrees Celsius", pKCO2_5
print "pK1 at 5 degrees Celsius", pK1_5
print "pK2 at 5 degrees Celsius", pK2_5
cacid_5 = 10**(-1*pKCO2_5) * CO2_med_atm
bicarb_5 = 10**(-1*pK1_5)*(cacid_5/H)
carb_5 = 10**(-1*pK2_5)*(bicarb_5/H)
print "Molar concentration of carbonic acid at 5 C =", cacid_5
print "Molar concentration of bicarbonate at 5 C =", bicarb_5
```

```
print "Molar concentration of carbonate at 5 C =", carb_5
```

#Note that carbonate makes up a small fraction of DIC; carbonate can be ignored from the code at the range of pH found in most natural rain water. But, for completion the full carbonate reactions are shown.

```
DIC_5 = cacid_5+bicarb_5+carb_5
DIC_5_mg = DIC_5*12*1000
print "Molar DIC at 5 C =", DIC_5
print "DIC (mg/L) at 5 C = ", DIC_5_mg
ecacid_5 = slope_H2CO3*5+intercept_H2CO3
ebicarb_5 = slope_HCO3*5+intercept_HCO3
ecarb_5 = slope_CO3*5+intercept_CO3
print 'Isotopic fractionation H2CO3-CO2(g) at 5 C =', ecacid_5
print 'Isotopic fractionation HCO3-CO2(g) at 5 C =', ebicarb_5
print 'Isotopic fractionation CO3-CO2(g) at 5 C =', ecarb_5
eDIC_5 = ecacid_5*cacid_5/DIC_5 + ebicarb_5*bicarb_5/DIC_5 + ecarb_5*carb_5/DIC_5
print 'Gross Isotopic fractionation DIC-CO2(g) at 5 C =', eDIC_5
```

#Code for carbonate equilibria at 10 degrees Celsius:

```
pKCO2_10 = KCO2_a*10**2 + KCO2_b*10+KCO2_c
pK1_10 = K1_a*10**2 + K1_b*10+K1_c
pK2_10 = K1_a*10**2 + K2_b*10+K2_c
print "pKCO2 at 10 degrees Celsius", pKCO2_10
print "pK1 at 10 degrees Celsius", pK1_10
print "pK2 at 10 degrees Celsius", pK2_10
cacid_10 = 10**(-1*pKCO2_10) * CO2_med_atm
bicarb_10 = 10**(-1*pK1_10)*(cacid_10/H)
carb_10 = 10**(-1*pK2_10)*(bicarb_10/H)
print "Molar concentration of carbonic acid at 10 C =", cacid_10
print "Molar concentration of bicarbonate at 10 C =", bicarb_10
print "Molar concentration of carbonate at 10 C =", carb_10
DIC_10 = cacid_10+bicarb_10+carb_10
DIC_10_mg = DIC_10*12*1000
print "Molar DIC at 10 C =", DIC_10
print "DIC (mg/L) at 10 C =", DIC_10_mg
ecacid_10 = slope_H2CO3*10+intercept_H2CO3
ebicarb_10 = slope_HCO3*10+intercept_HCO3
ecarb_10 = slope_CO3*10 + intercept_CO3
print 'Isotopic fractionation H2CO3-CO2(g) at 10 C =', ecacid_10
print 'Isotopic fractionation HCO3-CO2(g) at 10 C =', ebicarb_10
print 'Isotopic fractionation CO3-CO2(g) at 10 C =', ecarb_10
eDIC_10 = ecacid_10*cacid_10/DIC_10 + ebicarb_10*bicarb_10/DIC_10 + ecarb_10*carb_10/DIC_10
print 'Isotopic fractionation DIC-CO2(g) at 10 C =', eDIC_10
```

#Code for carbonate equilibria at 15 degrees Celsius:

```
pKCO2_15 = KCO2_a*15**2 + KCO2_b*15+KCO2_c
pK1_15 = K1_a*15**2 + K1_b*15+K1_c
```

```
pK2_15 = K1_a*15**2 + K2_b*15+K2_c
print "pKCO2 at 15 degrees Celsius", pKCO2_15
print "pK1 at 15 degrees Celsius", pK1_15
print "pK2 at 15 degrees Celsius", pK2_15
cacid_15 = 10**(-1*pKCO2_15) * CO2_med_atm
bicarb_15 = 10**(-1*pK1_15)*(cacid_15/H)
carb_15 = 10**(-1*pK2_15)*(bicarb_15/H)
print "Molar concentration of carbonic acid at 15 C =", cacid_15
print "Molar concentration of bicarbonate at 15 C =", bicarb_15
print "Molar concentration of carbonate at 15 C =", carb_15
DIC_15 = cacid_15+bicarb_15+carb_15
DIC_15_mg = DIC_15*12*1000
print "Molar DIC at 15 C =", DIC_15
print "DIC (mg/L) at 15 C =", DIC_15_mg
ecacid_15 = slope_H2CO3*15+intercept_H2CO3
ebicarb_15 = slope_HCO3*15+intercept_HCO3
ecarb_15 = slope_CO3*15 + intercept_CO3
print 'Isotopic fractionation H2CO3-CO2(g) at 15 C =', ecacid_15
print 'Isotopic fractionation HCO3-CO2(g) at 15 C =', ebicarb_15
print 'Isotopic fractionation CO3-CO2(g) at 15 C =', ecarb_15
eDIC_15 = ecacid_15*cacid_15/DIC_15 + ebicarb_15*bicarb_15/DIC_15 + ecarb_15*carb_15/DIC_15
print 'Isotopic fractionation DIC-CO2(g) at 15 C =', eDIC_15
```

#Code for carbonate equilibria at 20 degrees Celsius:

```
pKCO2_20 = KCO2_a*20**2 + KCO2_b*20+KCO2_c
pK1_20 = K1_a*20**2 + K1_b*20+K1_c
pK2_20 = K1_a*20**2 + K2_b*20+K2_c
print "pKCO2 at 20 degrees Celsius",pKCO2_20
print "pK1 at 20 degrees Celsius", pK1_20
print "pK2 at 20 degrees Celsius", pK2_20
cacid_20 = 10**(-1*pKCO2_20) * CO2_med_atm
bicarb_20 = 10**(-1*pK1_20)*(cacid_20/H)
carb_20 = 10**(-1*pK2_20)*(bicarb_20/H)
print "Molar concentration of carbonic acid at 20 C =", cacid_20
print "Molar concentration of bicarbonate at 20 C =", bicarb_20
print "Molar concentration of carbonate at 20 C =", carb_20
DIC_20 = cacid_20+bicarb_20+carb_20
DIC_20_mg = DIC_20*12*1000
print "Molar DIC at 20 C =", DIC_20
print "DIC at 20 C (mg/L) =", DIC_20_mg
ecacid_20 = slope_H2CO3*20+intercept_H2CO3
ebicarb_20 = slope_HCO3*20+intercept_HCO3
ecarb_20 = slope_CO3*20 + intercept_CO3
print 'Isotopic fractionation H2CO3-CO2(g) at 20 C =', ecacid_20
print 'Isotopic fractionation HCO3-CO2(g) at 20 C =', ebicarb_20
print 'Isotopic fractionation CO3-CO2(g) at 20 C =', ecarb_20
eDIC_20 = ecacid_20*cacid_20/DIC_20 + ebicarb_20*bicarb_20/DIC_20 + ecarb_20*carb_20/DIC_20
```

```
print 'Isotopic fractionation DIC-CO2(g) at 20 C =', eDIC_20
```

#Code for carbonate equilibria at 25 degrees Celsius:

```
pKCO2_25 = KCO2_a*25**2 + KCO2_b*25+KCO2_c
pK1_25 = K1_a*25**2 + K1_b*25+K1_c
pK2_25 = K1_a*25**2 + K2_b*25+K2_c
print "pKCO2 at 25 degrees Celsius",pKCO2_25
print "pK1 at 25 degrees Celsius", pK1_25
print "pK2 at 25 degrees Celsius", pK2_25
cacid_25 = 10**(-1*pKCO2_25) * CO2_med_atm
bicarb_25 = 10**(-1*pK1_25)*(cacid_25/H)
carb_25 = 10**(-1*pK2_25)*(bicarb_25/H)
print "Molar concentration of carbonic acid at 25 C =", cacid_25
print "Molar concentration of bicarbonate at 25 C =", bicarb_25
print "Molar concentration of carbonate at 25 C =", carb_20
DIC_25 = cacid_25+bicarb_25+carb_25
DIC_25_mg = DIC_25*12*1000
print "Molar DIC at 25 C =", DIC_25
print "DIC at 25 C (mg/L)", DIC_25_mg
ecacid_25 = slope_H2CO3*25+intercept_H2CO3
ebicarb_25 = slope_HCO3*25+intercept_HCO3
ecarb_25 = slope_CO3*25 + intercept_CO3
print 'Isotopic fractionation H2CO3-CO2(g) at 25 C =', ecacid_25
print 'Isotopic fractionation HCO3-CO2(g) at 25 C =', ebicarb_25
print 'Isotopic fractionation CO3-CO2(g) at 25 C =', ecarb_25
eDIC_25 = ecacid_25*cacid_25/DIC_25 + ebicarb_25*bicarb_25/DIC_25 + ecarb_25*carb_25/DIC_25
print 'Isotopic fractionation DIC-CO2(g) at 25 C =', eDIC_25
```

#Code for carbonate equilibria at 30 degrees Celsius:

```
pKCO2_30 = KCO2_a*30**2 + KCO2_b*30+KCO2_c
pK1_30 = K1_a*30**2 + K1_b*30+K1_c
pK2_30 = K1_a*30**2 + K2_b*30+K2_c
print "pKCO2 at 30 degrees Celsius", pKCO2_30
print "pK1 at 30 degrees Celsius", pK1_30
print "pK2 at 30 degrees Celsius", pK2_30
cacid_30 = 10**(-1*pKCO2_30) * CO2_med_atm
bicarb_30 = 10**(-1*pK1_30)*(cacid_30/H)
carb_30 = 10**(-1*pK2_30)*(bicarb_30/H)
print "Molar concentration of carbonic acid at 30 C =", cacid_30
print "Molar concentration of bicarbonate at 30 C =", bicarb_30
print "Molar concentration of carbonate at 30 C =", carb_30
DIC_30 = cacid_30+bicarb_30+carb_30
DIC_30_mg = DIC_30*12*1000
print "Molar DIC at 30 C =", DIC_30
print "DIC at 30 C (mg/L)", DIC_30_mg
ecacid_30 = slope_H2CO3*30+intercept_H2CO3
ebicarb_30 = slope_HCO3*30+intercept_HCO3
```

```
ecarb_30 = slope_CO3*30 + intercept_CO3
print 'Isotopic fractionation H2CO3-CO2(g) at 30 C =', ecacid_30
print 'Isotopic fractionation HCO3-CO2(g) at 30 C =', ebicarb_30
print 'Isotopic fractionation CO3-CO2(g) at 30 C =', ecarb_30
eDIC_30 = ecacid_30*cacid_30/DIC_30 + ebicarb_30*bicarb_30/DIC_30 + ecarb_30*carb_30/DIC_30
print 'Isotopic fractionation DIC-CO2(g) at 30 C =', eDIC_30

#This portion of the code combines the calculated DIC concentrations and eDIC-CO2 fractionations
#into a new table
temps = array([5,10,15,20,25,30])
DIC_temps = array([DIC_5_mg, DIC_10_mg, DIC_15_mg, DIC_20_mg, DIC_25_mg, DIC_30_mg])
eDIC_temps = array([eDIC_5, eDIC_10, eDIC_15, eDIC_20, eDIC_25, eDIC_30])
print temps
print DIC_temps
print eDIC_temps

#This portion of the code uses the eDIC-CO2 fractionation values to calculate the final d13C-DIC
#composition of rain water from 5 to 30 C
eDIC_CO2 = eDIC_temps + SGP_13CO2_med
print eDIC_CO2

#DIC concentration varies with temperature
#The code will output a figure of temperature vs DIC concentration
coeff_DIC = polyfit(temps, DIC_temps, 2)
model_DIC = poly1d(coeff_DIC)
model_DIC(temps)
plot(temps, DIC_temps, 'ko')
plot(temps, model_DIC(temps), 'k')
print "Coefficients for DIC", coeff_DIC
xlabel(r'Temperature ($\degree$C)',fontsize=13)
ylabel("DIC (mg/L)", fontsize=13)
xlim(0,35)
ylim(0.1,0.4)
savefig("rainDICvstemp.png")

#Isotopic fractionation between DIC and gaseous CO2 also varies with temperature
#The code will output a figure of temperature vs e13C-CO2-DIC enrichment
model_eDIC = poly1d(coeff_eDIC)
model_eDIC(temps)
plot(temps, eDIC_temps, 'ko')
plot(temps, model_eDIC(temps), 'k')
print "Coefficients for eDIC", coeff_eDIC
xlabel(r'Temperature ($\degree$C)',fontsize=13)
ylabel(ur'$\epsilon^{13}C_{DIC-CO_2(g)} (\u2030)$', fontsize=14)
xlim(0,35)
ylim(-.05,0.30)
tight_layout()
```

```
savefig("raineDICvstemp.png")

#DIC isotopic composition (d13C-DIC) also varies with temperature
#The code will output a figure of temperature vs d13C-DIC composition
coeff_eDIC_CO2 = polyfit(temps, eDIC_CO2, 2)
model_eDIC_CO2 = poly1d(coeff_eDIC_CO2)
model_eDIC_CO2(temps)
plot(temps, eDIC_CO2, 'ko')
plot(temps, model_eDIC_CO2(temps), 'k')
print "Coefficients for eDIC-CO2", coeff_eDIC_CO2
xlabel(r'Temperature ($\degree$C)',fontsize=13)
ylabel(ur'$\delta^{13}C-DIC (\u2030)$', fontsize=14)
xlim(0,35)
tight_layout()
savefig("raineDIC_CO2.png")
```