

# INVESTIGATIONS INTO THE POTENTIAL FOR HYPOGENE SPELEOGENESIS IN THE CUMBERLAND PLATEAU OF SOUTHEAST KENTUCKY, U.S.A.

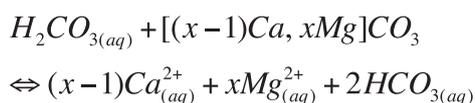
Lee J. Florea

Department of Geological Sciences, Ball State University, 2000 W. University Ave., Muncie, IN 47306, U.S.A.,  
lflorea@bsu.edu

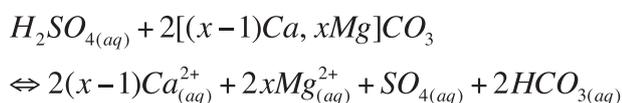
This manuscript offers preliminary geochemical evidence that investigates the potential for hypogene speleogenesis in the Cumberland Plateau of southeastern Kentucky, U.S.A. The region was traditionally considered a classic example of epigenic karst, but new insights have uncovered tantalizing observations that suggest alternatives to simple carbonic acid speleogenesis. Such first-order observations have included natural petroleum seeps at the surface and in caves, occasional cave morphologies consistent with action of hypogene fluids, and prolific gypsum within cave passages. To this point, geochemical data from caves and springs verify carbonic acid as the primary dissolutional agent; however, these same analyses cannot rule out sulfuric acid as a secondary source of dissolution. In this paper, Principal Component Analysis of ionic data reveals two components that coordinate with parameters associated with “karst water” and shallow brine. In contrast, molar ratios of  $\text{Ca}^+$  and  $\text{Mg}^+$  as compared to  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  closely follow the reaction pathway stipulated by the carbonate equilibria reactions. Despite these data, the role, if any, of hypogene speleogenesis in the karst of the Cumberland Plateau remains inconclusive. It is very likely that carbonic acid dominates speleogenesis; however, contributions from sulfuric acid may influence our understanding of “inception” and carbon flux within these aquifers.

## 1. Introduction

The chemistry of groundwater in karst aquifers reflects contributions from the dissolution of carbonate bedrock where the sources of acid come primarily from the reactions between water and dissolved carbon dioxide, which produces carbonic acid, or between dissolved oxygen and sulfide, which produces sulfuric acid. In the case of carbonic acid, the net chemical reaction yields equal contributions of dissolved inorganic carbon (DIC) from both soil/atmosphere and bedrock:

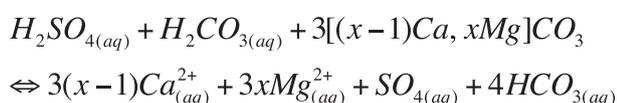


Note that the above reaction yields a 1:2 molar ratio of cations to bicarbonate in the products. Contrast this with the case of sulfuric acid, where the net reaction with the carbonate bedrock limestone reveals DIC derived solely from the bedrock:



In this reaction, note that the molar ratio between the cations and bicarbonate and between the cations and anions in the products is 1:1 and 2:3, respectively.

Finally, if we combine the two reactions above into a net reaction assuming equal contributions from carbonic and sulfuric acids, we arrive at the following:



that reveals a 3:4 molar ratio between the cations in solution and bicarbonate or a 3:5 ratio between the cations and anions in solution. It is important to mention that, when

assuming equal contributions from the two acids, only 25% of the DIC will originate from the soil/atmosphere. This testifies to the relative strength of the two acids.

The first of the above equations represents the “carbonic acid speleogenesis”, or CAS, model of cave development, where carbon-dioxide-enriched waters from percolating, epigenetic recharge react with the carbonate bedrock (Ford and Williams 2007; White 1988). Caves in southeastern Kentucky, U.S.A. serve in the literature as classic examples of epigenic karst (e.g., Simpson and Florea 2009). In these systems the chemical products of carbonate dissolution,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  (and as a result pH) are generally inversely correlated to discharge – as discharge goes up, the concentration of these ions (and therefore specific conductance – SpC) goes down due to, in part, dilution. This notwithstanding pulses of storage water pushed through at the beginning of storm events.

The second equation, in contrast, represents the “sulfuric acid speleogenesis” (Jagnow et al. 2000), or SAS, model of cave development. This model is used to explain, for example, the caves from the Guadalupe Mountains of New Mexico (Hill 1990) where sources of acidity arise from below – a “hypogene” model. Modern examples of SAS have been identified in Cueva de Villa Luz in Mexico (Hose et al. 2000), Grotte di Frasassi in Italy (Galdenzi and Menchetti 1995), the hydrothermal springs and caves in the Cerna River Valley (Wynn et al. 2010; Onac et al. 2011) in Romania, and Lower Kane Cave in Wyoming (Engel et al. 2004), among others. Re-appraisal of hypogenic theories based on hydrogeological definition has been done in Klimchouk (2007). Recent investigations in the Edwards aquifer in central Texas (e.g., Schindel et al. 2008) are an example of a region specific approach to understanding hypogene speleogenesis.

This brief paper explores the relationship between ions in solution and field chemistry in spring water from southeast

Kentucky. These data are analysed using two methods, Principal Component Analysis (PCA) and molar ratios to investigate the relative importance of the two reaction pathways, CAS and SAS, as they currently contribute to the development of cavernous porosity.

While there can be no doubt, *a priori*, that CAS dominates the current karst aquifers of southeast Kentucky, closer inspection of caves in these aquifers reveal features noted by Ewers (1985) where he popularized the term “paragenesis”, in which the bottom of the cave passage was the inception horizon and the dissolution progressed upward. Recent research on hypogene speleogenesis, in which rising fluids dissolve limestone, raises a question of whether the observed paragenetic features are in fact hypogene features.

For example, Florea et al. (2011a) document passage geometries within caves in southeast Kentucky located near shallow oil reservoirs in Mississippian strata that contain diagnostic features that are concordant with a SAS interpretation, such as rising half-tubes leading toward cupolas, blind passages, and possible bubble tracks (Klimchouk 2007). Some of these caves have identified petroleum seeps and curious passage names such as “sewer room”, “gasoline alley”, and “oil cave”. In fact, “dead oil” is clearly visible within cross-lamina of the Ste. Genevieve limestone of Redmond Creek Cave (Walden et al. 2007).

## 2. Physical Setting

Data come from the Cumberland Escarpment in southeast Kentucky along the east flank of the Cincinnati Arch, a broad saddle-shaped uplift aligned north-south in north-central Tennessee and south-central Kentucky. Erosion on the structural highs located in the Nashville Dome of Tennessee and the Jessamine Dome of central Kentucky have exposed Ordovician carbonates at the core of those domes. Progressively younger strata are revealed away from the center of those structural highs. The topography of the study area is split equally between uplands of the Cumberland Plateau and deeply incised valleys that drain those uplands. The terrain of the escarpment is rugged, with upper slopes lined with vertical cliffs of Pennsylvanian sandstones and conglomerates of the Lee Formation, a “bench” of gentle slopes marking the exposure of transitional-marine calcareous shale that comprise the upper-Mississippian Paragon Formation, and lower slopes and sinkhole floors underlain by the relatively pure carbonates of the middle-Mississippian Slade Formation (Ettensohn et al. 1984). Relief in the study area exceeds 230 m with ridge tops above 530 m and valley floors below 300 m elevation above sea level.

### 2.1. Karst Geology and Hydrology

The Slade Formation, regionally divided into the St. Louis, the Ste. Genevieve, and Kidder Limestone members, is significantly modified by solution activity, and karst landscapes dominate the area of carbonate exposure (Simpson and Florea 2009). Less soluble cross-bedded siltstones of the Salem-Warsaw Formations locally act as a base for conduit development below the Slade Formation.

Sinkholes and other closed drainage features prevail within incised valleys. Vertical solution shafts occur in stress release fractures along the hillsides (Ferguson 1967) near the contact with overlying siliciclastics and capture allogenic recharge from the plateau surface (Brucker et al. 1972). In the classic epigenic model applied to this region, vadose drainage through caves follows a stair-step pattern through the strata of the plateau margin (Crawford 1984) and coalesces into sinuous base-level conduits that generally parallel the surface valley and topographic contours (Sasowsky and White 1994). Tiers of these horizontal passages formed in response to episodic changes of base level controlled by the advance and retreat of the Laurentide ice sheet (Anthony and Granger 2004). Aquifer storage is concentrated in the rock matrix; however, the low permeability of these carbonates ensures that the communication between the matrix and the cave passages is low. Therefore, springflow hydrographs are “flashy” (White 1988; Florea and Vacher 2006) with most accessible storage lingering within the epikarst.

### 2.2. Spring Chemistry in Southeast Kentucky

Preliminary geochemical investigations by Dugan et al. (2012) provide a geochemical “snapshot” of water chemistry from fifteen karst springs distributed within the Otter Creek watershed southern Wayne County, Kentucky, USA – a tributary of the Cumberland River that contains sinking streams, sulfur seeps, integrated cave systems, and Kentucky’s largest sinkhole. The results cluster into three groups of springs, traditional karst springs, tufa springs, and sulfur seeps, that are in part spatially controlled by the Sunnybrook Anticline (Fig. 1). This anticline has an amplitude of approximately 30 m, is oriented N-NE, and is parallel to the trend of the Cumberland Escarpment.

Tufa springs represent the “most evolved” calcium-bicarbonate water on a geochemical pathway that connects meteoric water, recharge, traditional karst springs, and tufa springs Florea et al. (2011b). Waters at these tufa springs are supersaturated with respect to calcite and where they emerge, calcite precipitates. These springs probably resurge from long, strike-parallel flowpaths on the west flank of the anticline.

Sulfur seeps, with higher average SpC and temperatures (13.3 °C compared to 11.7 °C) are largely concentrated on the east flank of the anticline in the direction of the Appalachian Basin. The presence of these seeps is a manifestation of shallow petroleum reservoirs in lower Mississippian strata, particularly the Stray Sand pay zone, which consists of 3 to 10 m of cherty, geode-bearing limestone near the top of the Fort Payne 50 to 65 m above the Chattanooga shale (McFarlan 1943). These shallow reserves were exploited between the 1880s and the 1920s. Even though initial production in some wells was intense (upwards of 2,000 barrels of oil per day), production was generally short lived.

Sulfate/sulfide concentrations in the seeps are elevated and microbial-mediated sulfur redox is apparent as mats of microbial “slimes” at these seeps. Geologically, this setting is similar to that of Lower Kane Cave in the Mississippian-age Madison Limestone on the east flank of the Little Sheep

Mountain anticline in the Bighorn Basin of north-central Wyoming where sulfide-rich brines from nearby oil reservoirs are oxidized by bacterial-mats to induce SAS (Engle et al. 2004).

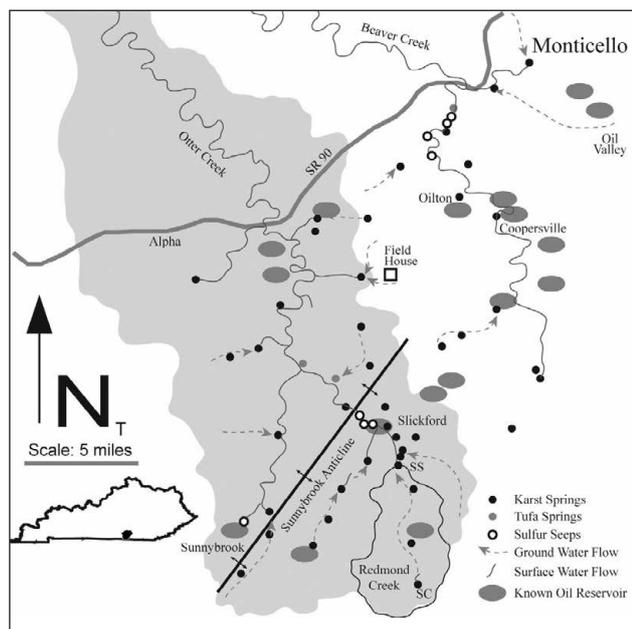


Figure 1. Study areas in Wayne County, KY, U.S.A. Index map of Kentucky illustrates the location of Wayne County. The Field House that serves as a base of operations is shown as an open square. The light gray is the Otter Creek Watershed with the Redmond Creek karst aquifer outlined in black. Sandy Springs and Stream Cave and indicated by SS and SC, respectively. The axis of the Sunnybrook Anticline is indicated as a black line. Principal communities are indicated in text. Groundwater flow paths are inferred by dye tracing and known cave survey. Oil reservoirs in shallow Mississippian-age strata identified by Abbott (1921) are denoted by gray ovals.

### 3. Methods

Samples come 15 springs in the Otter Creek watershed of southeast Kentucky, U.S.A. Two springs, Stream Cave and Sandy Springs, are one input to and the primary output from the Redmond Creek Karst Aquifer. Remaining sites comprise traditional karst springs, tufa springs, and sulfur seeps. Sixteen sets of bi-monthly samples were collected from Stream Cave and Sandy Springs during a detailed investigation in 2010–2011. The remaining sites comprise one or two samples collected between 2010 and 2012. Each sample was collected in two 250-mL HDPE bottles – an unpreserved sample for anions and a sample preserved with 2 mL of 6N HNO<sub>3</sub> for cations. All water samples were refrigerated at 4 °C until the time of analysis. Samples were analysed using Ion Chromatography and Inductively Coupled Plasma-Optical Emission Spectroscopy at the Waters Lab at Western Kentucky University. All results were reported in mg/L and converted to molar equivalents.

In the field, values of pH, SpC, Temperature, and Dissolved Oxygen were collected on site using an YSI multiparameter sonde. Alkalinity titrations were conducted onsite using a HACH ditital titrator and converted to molar equivalents of HCO<sub>3</sub><sup>-</sup>. Using the Debye-Hückle relationships the saturation state of the water with respect to calcite (C/C<sub>s</sub>) and the partial pressure of carbon dioxide (pCO<sub>2</sub>).

All data were compiled in a spreadsheet for analysis including computation of the molar ratios of species in solution. Of specific interest were those ratios outlined in the introduction that reveal the relative magnitudes of reaction pathways consistent with CAS and SAS. Secondly, the time-series data for each parameter collected at Sandy Springs were input into SPSS software. Factor analysis was applied to these data and resulting eigenvalues were weighted toward each input parameter.

## 4. Results and Discussion

### 4.1. Molar Ratios

Figure 2 is a cross plot of the molar concentration of Ca<sup>+</sup> and Mg<sup>+</sup> compared to the molar concentration of HCO<sub>3</sub><sup>-</sup>. Two trends are clear. The first is that all data from the traditional karst springs and from tufa springs generally fall along the 1:2 molar ratio line, clearly demonstrating the role of CAS in these systems. Sulfur springs, on the other hand, cluster closer to the 2:1 molar ratio line, which suggests enrichment in Ca<sup>+</sup> and Mg<sup>+</sup> without contemporaneous addition of HCO<sub>3</sub><sup>-</sup>. Such a trend is possible with entrainment of shallow brines. A cross plot between the Mg<sup>+</sup>/Ca<sup>+</sup> ratio as compared to Mg<sup>+</sup> helps provide further context (Figure 3). In this plot, data from Stream Cave, near the aquifer input and low in Mg<sup>+</sup>, have wide range in Mg<sup>+</sup>/Ca<sup>+</sup> ratios. Sandy Springs and the tufa springs, have near consistent Mg<sup>+</sup> concentrations and a stable Mg<sup>+</sup>/Ca<sup>+</sup> ratio between 0.16 and 0.2. This is consistent with dolomite abundance in the neighborhood of 12% to 15%. Sulfur seeps, with influence of shallow brines, have a wider span of Mg<sup>+</sup>/Ca<sup>+</sup> ratios and an increasing abundance of Mg<sup>+</sup> in solution.

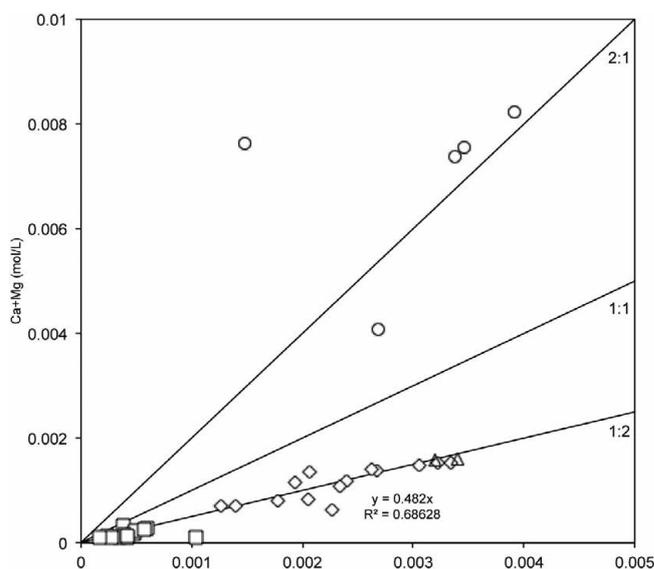


Figure 2. Molar ratios of Ca<sup>2+</sup> + Mg<sup>2+</sup> as compared against HCO<sub>3</sub><sup>-</sup>. Open squares are from Stream Cave, open diamonds are from Sandy Springs, open triangles are from tufa springs, and open circles are from sulfur seeps. Also shown are linear regressions that demonstrate molar ratios of 1:2, 1:1, and 2:1. The 1:2 and 1:1 linear regressions are an indication of dissolution of carbonate from carbonic acid and sulfuric acid, respectively.

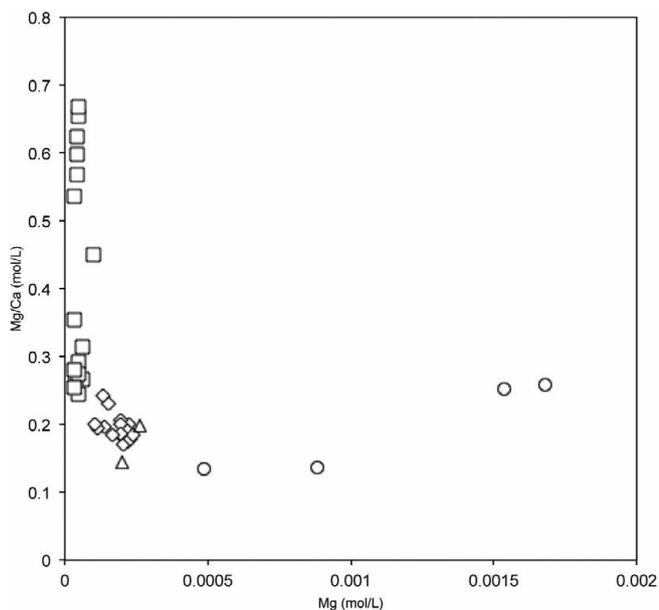


Figure 3. Cross plot of the molar ratio of  $Mg^{2+}/Ca^{2+}$  as compared against  $Mg^{2+}$ . Open squares are from Stream Cave, open diamonds are from Sandy Springs, open triangles are from tufa springs, and open circles are from sulfur seeps.

Figure 4 is a cross plot of the molar concentration of  $Ca^{2+}$  and  $Mg^{2+}$  compared to the molar concentration of  $HCO_3^-$  and  $SO_4^{2-}$ . Again, the sulfur springs cluster in a different locus than traditional karst springs or tufa springs, which still lay near the 1:2 molar ratio line, despite the addition of  $SO_4^{2-}$ . Interestingly, the data from the sulfur seeps, once corrected for the molar concentration of  $H_2S$ , cluster near the 1:1 molar ratio line.

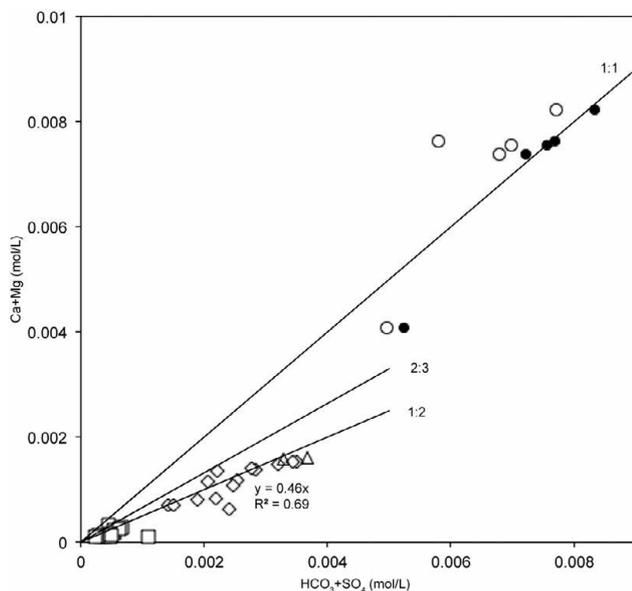


Figure 4. Molar ratios of  $Ca^{2+} + Mg^{2+}$  as compared against  $HCO_3^- + SO_4^{2-}$ . Open squares are from Stream Cave, open diamonds are from Sandy Springs, open triangles are from tufa springs, and open circles are from sulfur seeps. Filled circles are sulfur seeps with the addition of  $H_2S$ . Also shown are linear regressions that demonstrate molar ratios of 1:2, 2:3, and 1:1. The 1:2 linear regression is an indication of dissolution of carbonate from carbonic acid. The 2:3 linear regression is the expected molar ratio from dissolution sulfuric acid.

## 4.2. Principal Component Analysis of Karst Groundwater in Southeast Kentucky

Using PCA, a form of factor analysis in SPSS software, eigenvalues were derived that comprise the maximum amount of data variation (Florea 2012). In contrast to the method of molar ratios, the potential for SAS is revealed using PCA for the time series data of ion chemistry and field data for Sandy Springs. For example, when considering spring discharge (Q), dissolved ion concentrations, and the isotopic composition of DIC and rainwater, one PCA calculates that 48% of the variance can be explained by Q,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $NO_3^-$ , and  $HCO_3^-$ . A second component, including  $Na^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and total organic carbon (TOC) explains 31% of the variance. A final third component, comprising solely the isotopic composition of rainwater includes 10% of the remaining variance.

In a second, more restricted PCA, a first component comprises 48% of the variance and includes  $Ca^{2+}$ ,  $Mg^{2+}$ , the isotopes of DIC, and  $HCO_3^-$ , and a second component comprises 31% of the variance and includes  $SO_4^{2-}$ , the isotopes of DIC, and pH. Finally, a third PCA results in two components: a first including  $HCO_3^-$ ,  $Ca^{2+}$ , total dissolved solids (TDS) and Q for 53% of the variance, and a second with pH and  $SO_4^{2-}$  including 24% of the remaining variance. Component loading diagrams for these three PCA are included in (Figure 5).

Comparing these results to the original time-series data, the first component in each PCA corresponds to parameters that are inversely proportional to discharge; they vary according to interaction time with bedrock, namely limestone dissolution by CAS. In general, when discharge goes up, TDS, including  $NO_3^-$  from agricultural runoff, decreases because of dilution. The second component in these PCA includes parameters generally associated with brines and appears to be somewhat independent of discharge and perhaps directly related to pH. TOC is inversely proportional to these parameters suggesting that these brines have low organic content. The composition of DIC has complex loading on both components, suggesting that the isotopic composition of DIC may result in part from a blend of sources. Finally, the third component includes only the isotopic composition of rainwater, and as such suggests that rainfall composition is modulated external to the aquifer, a subject of a forthcoming publication (Florea, in review).

## 5. Summary Points

The available data presented in this paper reinforce our scientific understanding of the dominance of carbonic acid in the development of karst in southeast Kentucky, U.S.A. Molar fractions of cations and anions in groundwater samples from karst springs and tufa springs are consistent with the stoichiometry of the carbonate equilibria reactions. Results from PCA consistently reveal an eigenvalue comprised of variables associated with CAS in shallow groundwater that is anti-correlated to discharge. These results are neither revealing nor unexpected. However, the presence of sulfur seeps within caves and along base-level streams combined with morphologic features in caves associated with SAS evokes questions.

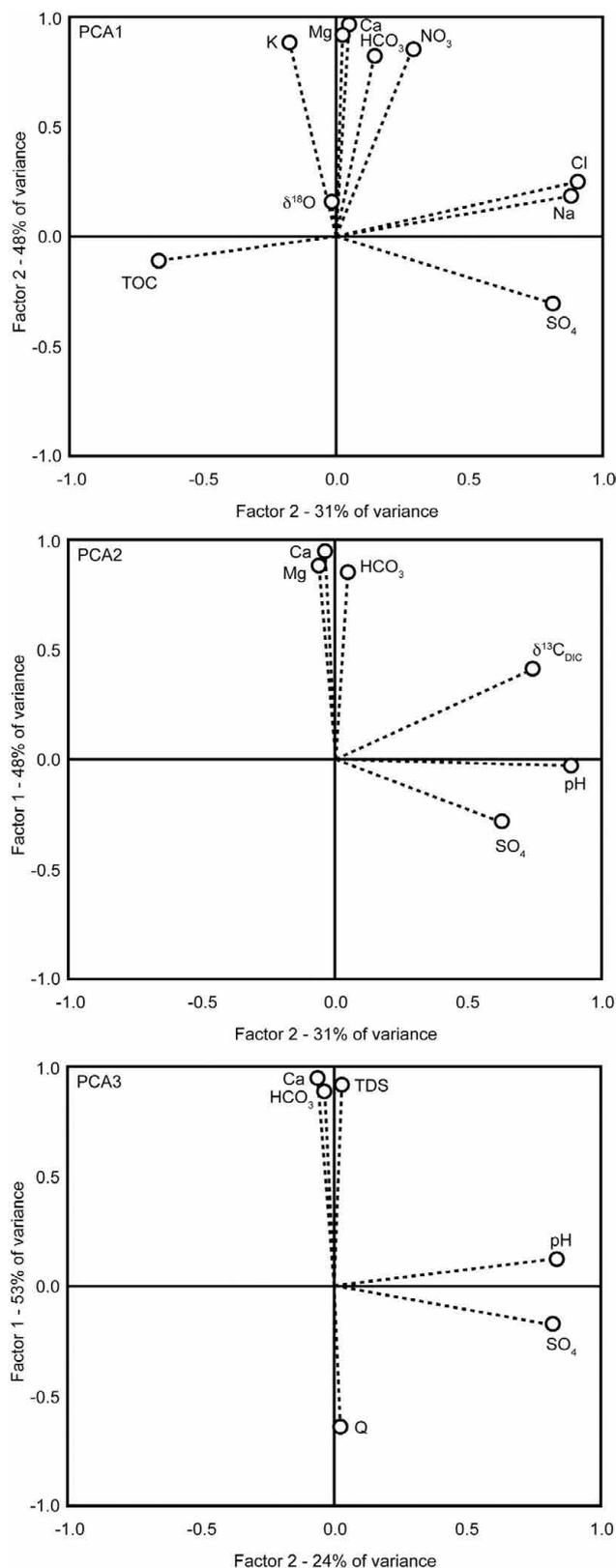


Figure 5. Principal component plots for PCA1, PCA2, and PCA3 showing the eigenvalue weighting of each variable. The percent of variance accounted for by each eigenvalue is given on the axis. Components of sample TDS associated with shallow groundwater are heavily weighted on eigenvalue 1 and are anti-correlated to discharge. Components of sample TDS associated with shallow brines are heavily weighted on eigenvalue 2 and are anti-correlated to TOC. pH co-varies with the shallow brines. The isotopes of DIC have complex loading.

Molar ratios clearly identify the sulfur seeps are being from shallow brines associated with shallow reservoirs of petroleum. Enriched in  $\text{H}_2\text{S}$ , these sites are likely experiencing SAS. The question remains as to how prevalent this process is (e.g., what is the relative magnitude of CAS and SAS). Such an investigation may influence our understanding of the “inception” period in these karst aquifers – the earliest stages of secondary permeability development – and the magnitude of carbon flux from these aquifers – specifically, the volume of inorganic carbon sequestered from the atmosphere and rhizosphere.

The data from Sandy Springs may lend some additional insight. For example, in each PCA, variables commonly associated with brines co-vary and account for a significant percent of the variance in the data. These data seem to vary independent of discharge and are anti-correlated to TOC. This could be a result of entrainment of shallow brines that are depleted in organic carbon within the karst aquifer. The isotopes of carbon in DIC within these samples exhibit complex loading on each eigenvalue. This suggests that contributions to DIC may come from both shallow groundwater where CAS dominates and from the entrained shallow brines where dissolved sulfides are oxidized creating the conditions for SAS on a limited scope. It is worth noting that at least one small sulfur seep has been identified within the cave that feeds Sandy Springs. Corroded bedrock in the vicinity of this seep is a clear indication of SAS on at least the scale of individual seeps. Recent measurements of isotopes of DIC from sulfur seeps in the Otter Creek watershed (Florea, et al. 2011c) demonstrate an enrichment of lithospheric carbon as would be expected from the stoichiometry of the SAS reaction presented in this manuscript.

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