

# Inorganic Carbon Flux and Aquifer Evolution in the South Central Kentucky Karst

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## Abstract

The geometries of carbonate karst aquifer "plumbing systems", and the rates at which they evolve, depend on the fluxes of water and CO<sub>2</sub> through them. A one-year, high temporal resolution study of flow and carbonate chemistry within the humid-subtropical Mammoth Cave System's Logsdon River quantifies significant variations in these fluxes over storm and seasonal time scales. Undersaturated storm waters dissolve rock within a 25-30 m thick flood zone. Waters were only undersaturated, and thus capable of dissolving the aquifer framework, 31% of the year. Rates of aquifer evolution are thus strongly influenced by time-varying processes. Although flood conditions occur during a small percentage of the time, they dominate chemical passage enlargement. Of the  $7.8 \times 10^3 \pm 1.9 \times 10^3$  kg ha<sup>-1</sup> of total inorganic carbon leaving the river's 25 km<sup>2</sup> catchment during the year, 1% entered the aquifer as recharge, 57% was derived from carbonate mineral dissolution, and 42% was produced by biological activities. Comparison of sources of inorganic carbon suggests that during large floods the aquifer is "rinsed" of the diffuse limestone dissolution products that accumulate during more normal conditions by waters moving downwards through the vadose zone. A dual approach, coupling quantitative modeling with calibration and refinement of the models by careful measurement of processes within real karst aquifers, provides a framework for developing a comprehensive understanding of karst system behavior.

## Introduction

Because of the low flow resistance typical of well-developed karst aquifers, significant changes in both flow and groundwater chemistry, and associated water-rock interactions, occur over a variety of timescales. Under some conditions these changes can be rapid. Since aquifer dissolution rates, in turn, depend on the spatial and temporal variations in the chemistry of the through-flowing waters, investigating the nature of these changes is necessary to understand karst aquifer and landscape development. Using a new method that provides high frequency quantification of important carbonate water chemistry parameters, this paper reports on the results of a one year sampling program (May 5, 1995 to May 4, 1996) designed to understand rates and magnitudes of water and carbon dioxide fluxes within one of the major underground rivers of the humid-subtropical south-central Kentucky karst aquifer. Using this information we evaluate how these changes, at time scales ranging from minutes to months, impact conduit evolution and inorganic carbon transport through the aquifer. This work is being undertaken in cooperation with the International Geological Correlation Program, Project 379: "Karst Processes and the Global Carbon Cycle."

## Field Site

Logsdon River is one of the major underground streams of south-central Kentucky's Mammoth Cave karst aquifer (Figure 1). Within the Proctor Cave section of the system, near the south-western known edge of the Mammoth Cave System, Logsdon River converges with Hawkins River, which drains about 75 km<sup>2</sup> near Park City, Kentucky. Logsdon River drains the 25 km<sup>2</sup> Cave City groundwater basin. Within Logsdon River, about 100 m upstream from the confluence of the two rivers, are two 15-cm diameter, 145-m deep observation wells intersecting the river (Figure 1). One well is equipped with a compressor-driven pump for collecting water samples from the surface, and through the other electronic probes deliver high-resolution (two-minute) data on stage, velocity, temperature, and specific conductance. The bottoms of the wells can be reached underground (for pump and probe installation and maintenance) through the Doyel Valley Entrance to Mammoth Cave, requiring a 3-km round-trip through the cave. The conduit at the Logsdon River well site is about 3 m tall and 7 m wide, and lies near the downstream end of one of the world's longest known sections of accessible underground river passage, continuously traversable for over 8 km.

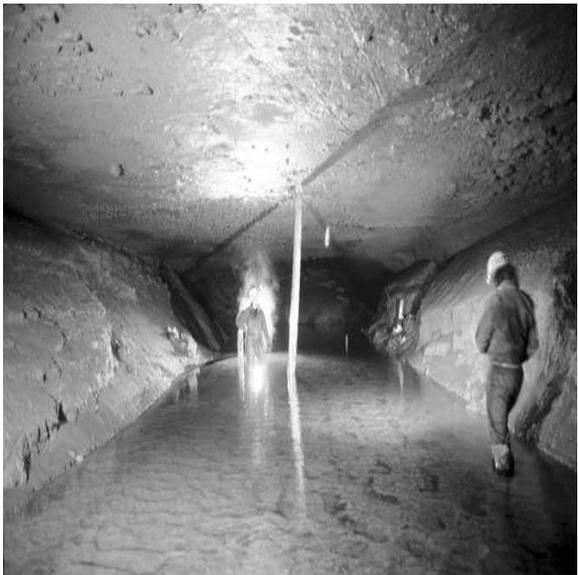


Figure 1. Field site at Logsdon River, the main trunk flow path of the Cave City Basin of the Mammoth Cave karst aquifer. Another well just out of the picture to the left of the passage delivers probes that record flow and chemical conditions of the river with two-minute resolution. Photos by Chris Groves.

## Methods

The primary objective of the research has been to collect sufficient high-resolution data on both flow and chemical characteristics of the river to quantitatively evaluate the magnitudes and rates of change of carbonate chemistry and water/rock interactions at a variety of time scales. Four probes are installed through the wells into each stream, including temperature, specific conductance, river stage, and velocity. A Campbell CR10 multi-channel data logger queries the probes every thirty seconds, and averages these readings every two minutes. Using an accurately surveyed passage cross-section at the well site, stage data were used to calculate flow cross-sectional area for discharge calculations.

With data resolution varying from two minutes during storms to hourly during static conditions (in the interest of both data storage and computational efficiency), these values were determined for 21,473 observations between May 5, 1995 to May 4, 1996. Equipment problems led to a loss of 19.9 days (5.4% of the period) of conductance data during the year. With the large number of conductance chemographs during storms available over the rest of our study period, however, we were able to closely estimate these missing periods using a procedure analogous to unit hydrograph analysis (Chow, 1964). In addition, electrical problems created offsets of the data (29.2 days, or 8.0%) that were corrected by calibration and translation. We used direct velocity measurements (with two minute resolution) to estimate discharge under open channel conditions, but these were limited by measurement at a single location in the center of the flow cross-section in each stream. To account for the vertical velocity distribution the velocity at 0.6 flow depth, which has been shown to be close to the mean velocity in the vertical profile, was related to the apparent velocity at the fixed-depth point of measurement assuming a logarithmic velocity distribution (Chow, 1959). In order to correct for longitudinal velocity variations, discharge measurements were made on eight occasions using standard wading-rod gaging techniques and a 0.3 meter longitudinal spacing (Chow, 1959), and the average ratio between mean and maximum velocity (assumed at the center of each channel, where the velocity sonde is located) was determined. The vertically corrected apparent velocity in each stream was then multiplied by this ratio (0.57).

Hourly water chemistry measurements have been made during storms of various magnitudes by sampling from the surface through the wells. Calcium has been

measured with either titration or with a Varian Spectra 10/20 atomic absorption spectrophotometer (AA) at the Ogden Environmental Water Lab at Western Kentucky University, and magnesium has been measured exclusively with atomic absorption. Samples for dissolved calcium and magnesium AA analysis were filtered (0.45  $\mu\text{m}$ ) and acidified. Conductivity and pH were measured immediately after sample collection. A gel filled combination electrode using two-point calibration was used to measure pH. Bicarbonate alkalinity was measured by acid titration either immediately after collection, or in some cases samples were stored on ice, and the titrations were done at the Ogden Laboratory within 24 hours.

## Analysis

With this information we have used least-squares regression analysis (Draper and Smith, 1981) to relate high-resolution specific conductivity data from within the river to calcium, magnesium, and bicarbonate concentrations, as well as pH (Figure 2). These relationships, along with direct temperature measurement, then allow calculation of several important components of carbonate system behavior with high temporal resolution, including  $\text{CO}_2$  pressures, dissolution rates, and total inorganic carbon (TIC) fluxes through the aquifer contributed from atmospheric, mineral, and biological sources.

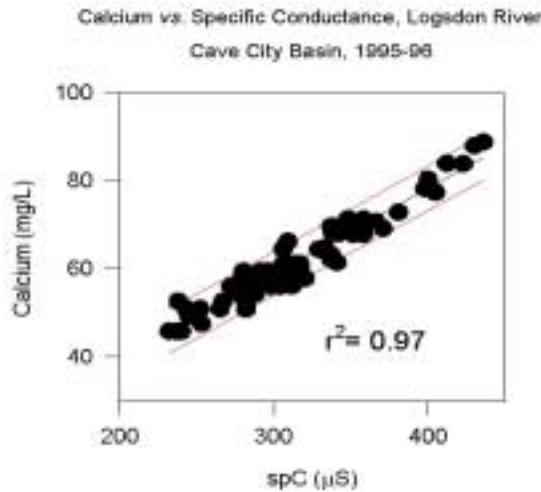


Figure 2. Statistical relationship between calcium and continuously measured specific conductance (spC) used in carbonate chemistry calculations.

Activities of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  are first obtained using the extended Debye-Hückel limiting law (Stumm and Morgan, 1981). Then activities of  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{CO}_3^*$  are calculated using appropriate equilibria, where

$$[\text{H}_2\text{CO}_3^*] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_1} \quad (1)$$

and

$$[\text{CO}_3^{2-}] = \frac{K_2[\text{HCO}_3^-]}{[\text{H}^+]}, \quad (2)$$

with activities indicated by square brackets. These are then summed with bicarbonate activities to obtain TIC for each observation, where

$$\text{TIC} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3^*], \quad (3)$$

where  $\text{H}_2\text{CO}_3^*$  is the sum of  $\text{H}_2\text{CO}_3^0$  and aqueous  $\text{CO}_2$  (Stumm and Morgan, 1981).

Calcite dissolution rates assumed reaction-limited kinetics and were calculated for each observation using the rate law of Plummer *et al.* (1978), where

$$\begin{aligned} \text{Rate} = & k_1[\text{H}^+] + k_2[\text{H}_2\text{CO}_3^*] + k_3[\text{H}_2\text{O}] \\ & - k_4[\text{Ca}^{2+}][\text{HCO}_3^-], \end{aligned} \quad (4)$$

with *Rate* expressed in mass of mineral lost per time per surface area of fluid/mineral contact, and where the *k*'s are temperature dependent kinetic rate constants (Plummer *et al.*, 1978). For ease of interpretation, we report results in this paper in the rate of conduit wall retreat (mm/yr) following the example of Palmer (1991).

We also investigate aquifer hydrochemical/evolution characteristics using a recently developed method to discriminate between the various sources of inorganic carbon cycling through karst aquifers (Groves and Meiman, 2000). In this analysis we assume that there are three classes of sources for total inorganic carbon, TIC, leaving a limestone or dolomite karst groundwater basin:

- a. dissolved inorganic carbon in precipitation, in equilibrium with the atmospheric background CO<sub>2</sub> pressure, entering the aquifer as recharge,  $C_a$ ,
- b. biological processes that produce gaseous CO<sub>2</sub> in the soil, vadose, and saturated zones, including microbial respiration, oxidation of organic material, and plant root respiration,  $C_b$ , and
- c. carbonate mineral dissolution,  $C_m$ .

Thus over a specified time interval  $t$ ,

$$\int_0^t TIC dt = \int_0^t C_a dt + \int_0^t C_b dt + \int_0^t C_m dt. \quad (5)$$

Since  $C_a$  and  $C_b$  originate in the atmosphere as CO<sub>2</sub> gas, and leave the karst system as dissolved inorganic carbon species, we define the inorganic component of the CO<sub>2</sub> sink,  $\xi$  due to flow and biogeochemical processes within the karst landscape/aquifer system:

$$\xi = \left( \int_0^t C_a dt + \int_0^t C_b dt \right) / tA \quad (6)$$

where  $t$  is the length of the sampling period, and  $A$  is drainage basin area.

$C_a$  is estimated by calculating a carbon mass flux leaving the basin, using measured river discharge and assuming  $TIC$  in equilibrium with a constant representative atmospheric CO<sub>2</sub> pressure, nominally set at 360 parts per million over the study period, using (3). In the current study, input data with two-minute resolution of chemical and flow conditions within the river are able to encompass all significant features of storm-scale and seasonal variations, so that close estimates of the appropriate integrals can be obtained.

To obtain both  $C_m$  and  $C_b$ , we make use of the fact that during dissolution of limestone or dolomite one mole of C is released from the mineral for each mole of Ca<sup>2+</sup> + Mg<sup>2+</sup>, regardless of the elementary reaction involved (Plummer *et al.*, 1978; Busenberg and Plummer, 1982), so that

$$\int_0^t C_m dt = \int_0^t (Ca^{2+} + Mg^{2+}) dt, \quad (7)$$

and by substituting (7) into (5) and rearranging,

$$\int_0^t C_b dt = \int_0^t TIC dt - \left( \int_0^t (Ca^{2+} + Mg^{2+}) dt + \int_0^t C_a dt \right). \quad (8)$$

## Results

### Flow and Chemistry Variations

Fifty-six storm events caused measurable changes in the flow or chemistry within the river during the study (Figure 3), with thirteen of the storms flooding the conduit to the ceiling. During the largest storm, on May 18, 1995, the water level reached a maximum height of 28.2 m, with a maximum rate of rise of 6.03 m/hr. The ceiling of the conduit under these conditions is about 25 m below the water table, and the conduit remained totally flooded for 114 hours. Based on observed flow characteristics, the year can be divided into a dry and wet season (Figure 3). After the May 1995 flood subsided, the conduit flooded only twice over the next 224 days, and one of those events was the remnants of a hurricane (Opal, study day 141, October 5), a relatively infrequent weather condition for Kentucky. In contrast, during the last 135 days of the study, beginning on Jan 2, 1996, floodwaters filled the conduit ten times, or an average of about once every two weeks.

The chemistry of the system also showed a seasonal signature (Figure 3), with the most highly concentrated fluids during the dry season, presumably reflecting a larger proportion of diffuse flow, in contrast to more diluted storm flow, with higher concentrations of dissolved limestone. A third-order regression curve of the 21,473 dissolution rate observations shows a sine-like form, apparently reflecting a higher frequency of storms during the winter and spring which do not allow the river's waters to return to a "chemical baseflow" condition, in which river flow is completely maintained relatively concentrated diffuse flow waters. Dissolution rates, in contrast, continue to fall for several months between the infrequent rains of the dry summer period. This suggests that the full relaxation time for the waters to reach a "chemical baseflow" condition in the river is on the order of months, rather than days in the case of river stage.

The maximum dissolution rates (associated with minimum conductivities) reached as a result of storms

nearly all fell within a close range, suggesting a maximum bounding value of about 1 mm/yr, associated with conductivity values of 190  $\mu\text{S}$  that, for sufficiently large rainfalls, is independent of season, rainfall amount, and antecedent moisture conditions. The one exception is the large May 1995 flood, where the conductivity reached a low of 167  $\mu\text{S}$ .

A striking feature is that the waters were oversaturated (negative values in Figure 3) about 69% of the year, so that dissolution took place only about one-third of the time (Groves *et al.*, 1999). Sampling upstream from this location to explore the geochemical evolution of Logsdon River (Anthony, 1998) suggests that  $\text{CO}_2$  outgassing along the stream is responsible for this oversaturated condition. Our data suggest that  $\text{CO}_2$  pressures at this point in the river system, in the lower end of the basin, are influenced primarily by the relative contributions of high  $\text{PCO}_2$  recharge from discrete inputs and during storms and lower  $\text{PCO}_2$  diffuse flow inputs. The latter have been in close, prolonged contact with limestone, and much of the gas has been consumed by the resulting carbonate mineral dissolution. This seasonality in  $\text{CO}_2$  pressures, and thus dissolution rates, is more closely in phase with seasonal hydrologic changes (including the influence of both precipitation

and evapotranspiration rates) than changes in seasonal soil  $\text{CO}_2$  levels, which are in general highest in the warm seasons (Miotke, 1974).

This oversaturated condition might suggest that the dissolution occurring during storms and the wet spring season is offset by mineral precipitation in the conduit during dryer periods. In fact, the mean rate over all 21,473 observations is -0.13 mm, indicating net precipitation over the year. Several observations, however, suggest that precipitation is limited. It has been reported in other settings that calcite saturation index (*SI*) values on the order of about +1 are required to exceed kinetic thresholds required for the initiation of calcite precipitation (*e.g.*, Herman and Lorah, 1988), and the maximum calculated *SI* values during the study period were less than 0.7. No macroscopic physical evidence of travertine deposition, such as rimstone dams, is present at the site. We have examined bed sediment grains collected at the end of the fall dry period (October, 1996) (Smith, *et al.*, 1997) under a scanning electron microscope, and washed sediment in acid to identify increased calcium concentrations, and have found evidence for minor calcite coatings. It is not clear, however, whether this precipitation occurred at the site, or when the grains were further upstream, where rimstone is common in some areas. Making the assumption that solutions do not become sufficiently oversaturated during the year to initiate calcite precipitation at the site (Figure 4), by setting all negative rates to zero, the mean calculated rate becomes 0.36 mm/year of dissolution. In either case, the importance of storm flows in dominating conduit enlargement is clear.

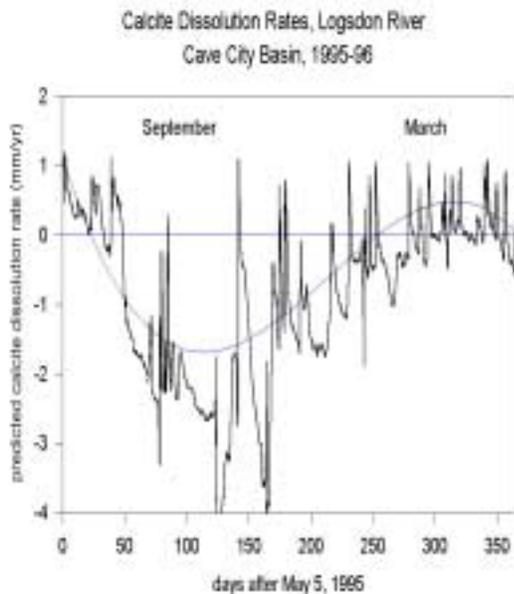


Figure 3. Predicted calcite dissolution rates showing both storm and seasonal scale variations, based on the rate law of Plummer *et al.* (1978). Negative values indicate mineral precipitation.

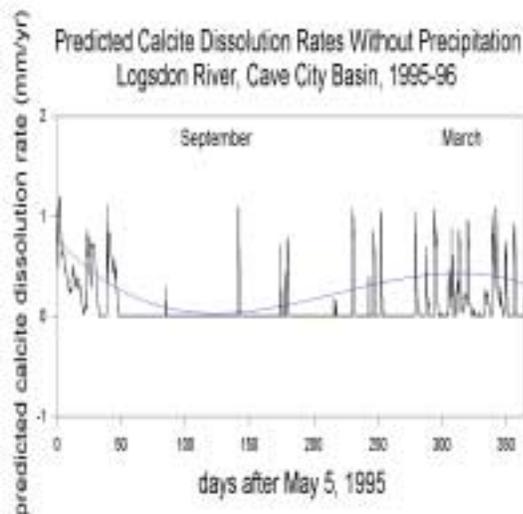


Figure 4. Predicted calcite dissolution rates based on the rate law of Plummer *et al.* (1978), assuming that kinetic barriers for precipitation are not met, and thus that the dissolution rate goes to zero during periods of oversaturation.

### Inorganic Carbon Budget and Transport Processes

Groves and Meiman (2000) measured the relative sources of the inorganic carbon flux in transport through the system over the study period discussed in this paper (eqs. (5)-(8)), and found that of the  $7.8 \times 10^3 \pm 1.9 \times 10^3 \text{ kg ha}^{-1}$  of total inorganic carbon leaving the  $25 \text{ km}^2$  Cave City Basin during the year, 1% entered the aquifer as recharge, 57% was derived from carbonate mineral dissolution, and 42% was produced by biological activities. Further interpretation of those data can reveal details of aquifer transport processes. It is the flux of water and carbon dioxide through the system that ultimately controls the evolution of the aquifer framework.

The magnitudes of the total inorganic carbon flux as well as those from mineral and biological sources were summed over each of the twelve months of the study period and plotted against mean monthly discharge for the same period (Figure 5).

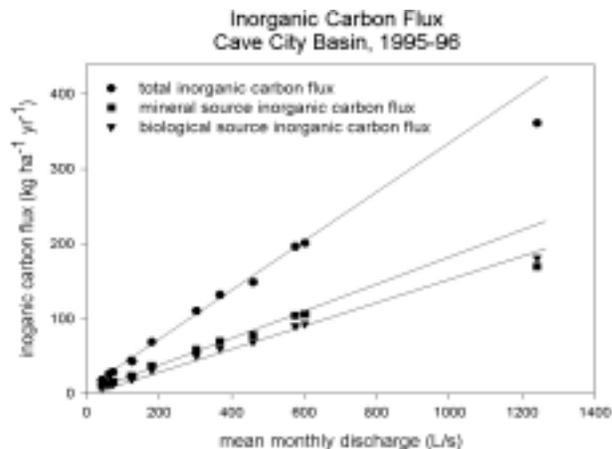


Figure 5. Magnitudes of inorganic carbon fluxes and discharge summed over monthly intervals.

In general, they show a nearly linear relationship, except for the point from May, 1995, which was dominated by a major flood, produced by roughly 25 cm of rainfall over less than one day (rightmost point on Figure 5), causing a stage increase of more than 28 m in twelve hours at the study site. In particular, the May point is in line with the biological source inorganic carbon (triangles on Figure 5), but that produced by dissolution of the carbonate bedrock falls far below the regression line for the eleven smaller flows. This suggests, first, that the inorganic carbon washed through the system produced by biological processes in the soil and vadose zone (Atkinson, 1977; Wood and Petraitis, 1984; White, 1988) occurs in an abundant enough supply that the amount transported through the system is roughly proportional to the amount of water available. In contrast, in May there is a clear deficit of mineral source carbon from that expected if the same relationship holds (Figure 6). A plausible explanation is that for most flows mineral carbon from diffuse parts of the vadose zone washes through the aquifer in proportion to the flow of water, but in sufficiently large flows this carbon is "rinsed" from the aquifer, and the water that follows becomes correspondingly diluted with respect to the products of dissolved limestone. The fact that this more dilute water should be significantly more undersaturated with respect to limestone than typical flows further highlights the dominant role that large storms appear to have on karst aquifer development.

The conclusions drawn from this carbon budgeting process do not consider the impacts of organic carbon, and thus may be influenced accordingly. We are currently beginning to investigate both organic carbon transport and microbial ecology of the Mammoth Cave karst aquifer (Elliott *et al.* 2000, and Vaughn, 1998) to

better understand and quantify carbon dynamics and how these may influence aquifer evolution.

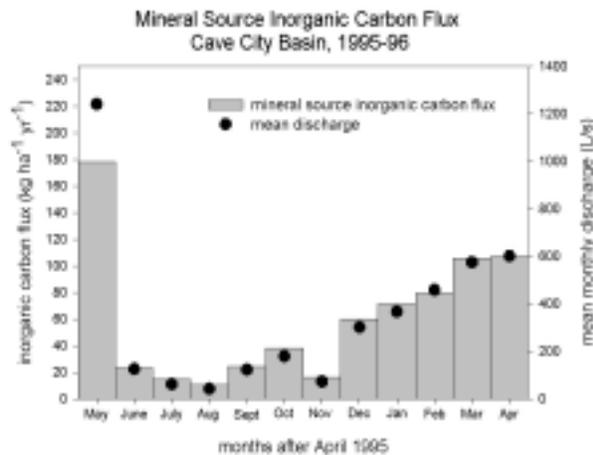


Figure 6. Mineral source organic carbon and discharge summed over monthly intervals.

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