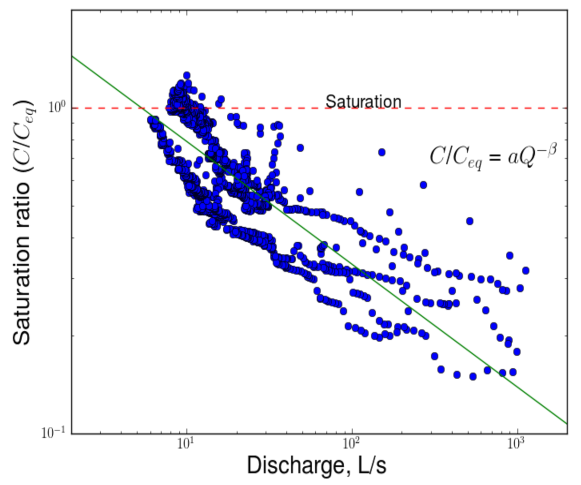
Characterization of solute-discharge relationships in springs and rivers in eogenetic and telogenetic karst aquifers

M.D. Covington (University of Arkansas) and J.D. Gulley (University of Texas)

Background

Temporal variability in solute-discharge relationships in rivers and springs in karst aquifers is often analyzed to obtain information about the behavior of karst systems, because such relationships should vary as a function of aquifer structure, recharge mode, and climatic factors. Solute-discharge relationships, the controls of which are still poorly understood, are also of active interest to the broader hydrology community (e.g. Godsey et al. 2009). In karst settings, previous work has suggested that discharge hydrographs from eogenetic and telogenetic karst springs display different characteristic behaviors, with eogenetic springs producing more muted and broad responses, and telogenetic springs producing sharper, more peaked responses (Florea and Vacher, 2005). These different hydrograph responses reflect key differences in residence time of recharge in aquifers. Because solute-discharge relationships also depend upon residence time distribution, eogenetic and telogenetic systems may also have characteristic differences in solute discharge-relationships. Temporal variations in the saturation index (SI) of calcite are of particular interest in karst, as these will be an important factor in determining the rates of incision of cave and surface streams through soluble carbonate strata. The current generation of speleogenesis models ignore the effects of variations in saturation state over time, even though a variety of studies have demonstrated their importance (e.g. Groves and Meiman, 2005; Palmer, 2007). One reason for this shortcoming is that, while previous studies have examined the variations in saturation at one or a few sites within a given region, no studies have attempted a broad characterization of these variations and the factors that control them across a wide range of lithological, climatic, and hydrological settings.

SI-Discharge Relations: an example case from a continuous monitoring study



Saturation state as a function of discharge for the stream in Lekinka Cave, an allogenically recharged cave stream near Postojna, Slovenia. Saturation varies strongly as a function of discharge. Hysteresis during rising and falling limbs of storms accounts for much of the observed scatter.

Leveraging legacy data

The USGS maintains a long record of publicly accessible water quality data (more than 100,000 samples from 1000's of sites). This data is made available via web services through the National Water Information System (NWIS). Additionally, water quality samples can be correlated against discharge records from USGS stream gauges. For this study we selected a set of 32 river and spring sites in karst settings across the U.S. that each had a substantial number of water quality samples appropriate for calculation of the SI of calcite. Additionally, we limited the selection to locations where information was available about the geological setting of the recharge area.

The 32 spring and river sites used in this study.

Automating the analysis process

In order to facilitate the analysis of a **large number of samples** (nearly 3,000), we developed scripts in python to automate the process. Our new python toolkit allows:

- automated download of water quality data given a list of USGS sites or an xml resulting from a query on the NWIS webpage
- filtering of samples that have poor quality or insufficient data for SI calculation
- processing of each sample through PHREEQC in order to obtain species activities and saturation indicies and reading out this data from the PHREEQC output files
- automated downloading of discharge values for each sample date
- plotting and statistical analysis of the data from each site
- analysis tools to compare sites and examine relationships between them

We are currently in the process of expanding the capabilities of the toolkit and developing a more friendly user interface. Ultimately, the code will be made available online (**http://www.speleophysics.com**).

Overarching Question: What factors control the relationship between discharge and SI?

Hypothesis 1: The recharge conditions (autogenic vs. allogenic) are the primary control.

Previous work has shown that the nature of recharge, either allogenic (coming from non-carbonate rocks) or autogenic (coming through carbonates), is strongly correlated to the extent of chemical variability of karst springs (Worthington et al. 1992).

Hypothesis 2: The geological history and matrix permeability are a strong control.

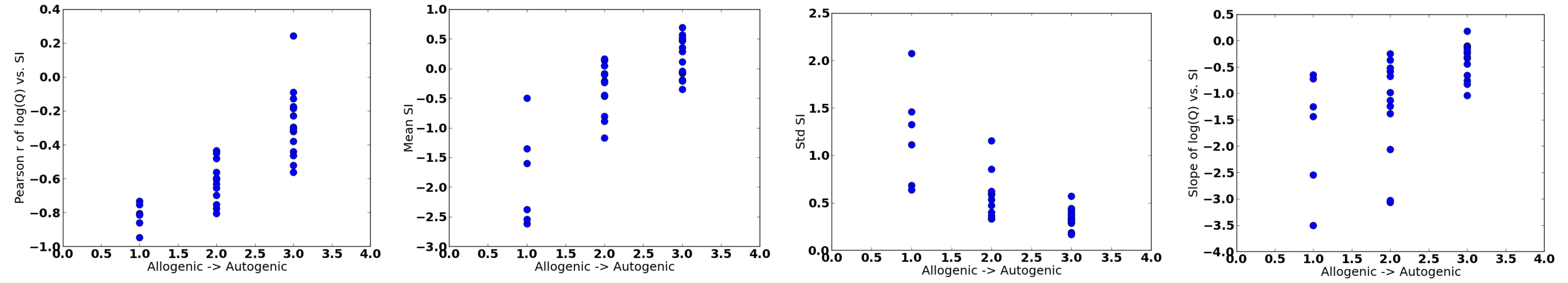
In eogenetic and telogenetic settings, matrix permeabilities are dramatically different, having important consequences for the amount of exchange between conduits and the matrix and the distribution of residence times within the aquifer. Eogenetic and telogenetic settings have been shown to display characteristic hydrograph properties and chemographs could be similarly influenced.

Site Classification

In order to test these hypotheses, we classified each site according to geological and recharge setting. Each site was classified as either **telogenetic (0) or eogenetic (1)**. In practice, all eogenetic sites were in Florida. We consulted technical reports and previous studies of spring recharge areas in combination with geological maps of surface basins in order to give each spring or river site a coarse recharge classification of: **1 – allogenic, 2 – mixed, or 3 – autogenic,** roughly dividing recharge proportions into thirds.

Allogenic vs. Autogenic Recharge

1 = mostly allogenic
2 = mixed
3 = mostly autogenic



Correlation coefficient between log(discharge) and the saturation index of calcite at each site

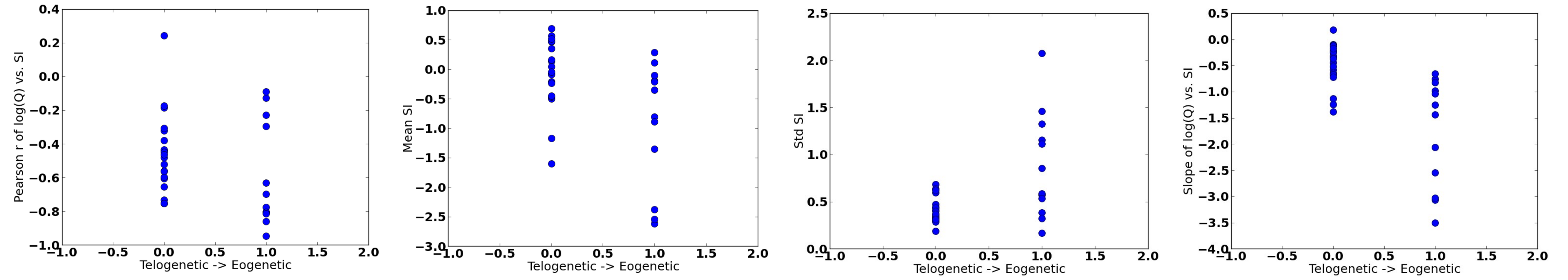
Mean saturation index of calcite at each site.

Standard deviation of the saturation index of calcite at each site.

Slope of the relationship between log(discharge) and the saturation index of calcite at each site.

Telogenetic vs. Eogenetic Karst

0 = telogenetic
1 = eogenetic



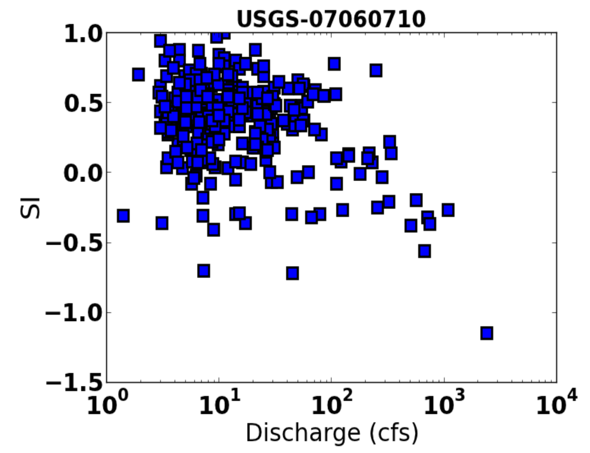
Correlation coefficient between log(discharge) and the saturation index of calcite at each site

Mean saturation index of calcite at each site.

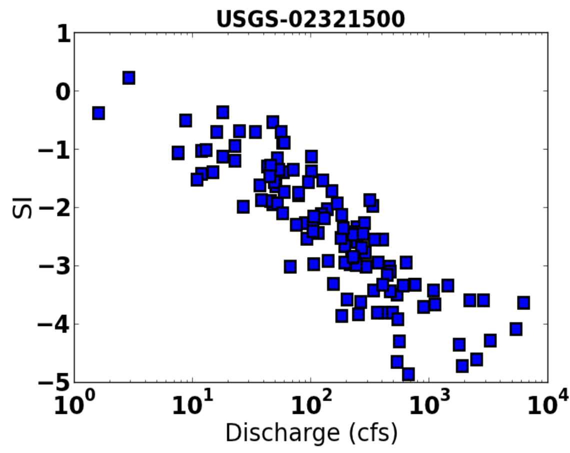
Standard deviation of the saturation index of calcite at each site.

Slope of the relationship between log(discharge) and the saturation index of calcite at each site.

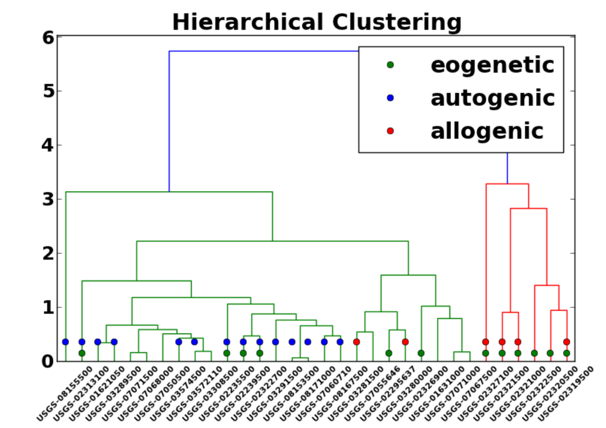
SI vs. Discharge at two example sites



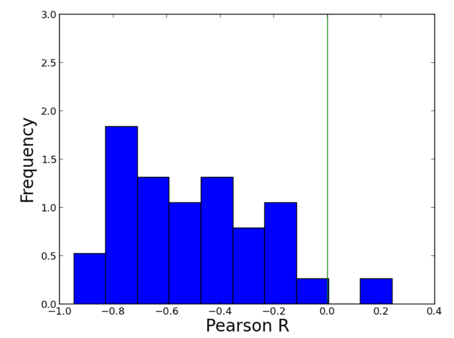
N. Fork Sylamore Ck., AR(autogenic, telogenetic)



Santa Fe Rv. @ Worthington Spring, FL (allogenic, eogenetic)



Clustring dendogram calculated using a weighted distance measure based on the 4 parameters above. Allogenic and autogenic sites cluster more closely than eogenetic and telogenetic sites.



Histogram of correlation coefficients between SI and Q for all 32 sites

References:

Florea, L.J. and H.L. Vacher (2005), Springflow Hydrographs: Eogenetic vs. Telogenetic Karst, *Ground Water*, 44, 3, 352-361.

Godsey, S.E., Kirchner, J.W., and D.W. Chow (2009), Concentration–discharge relationships reflect chemostatic characteristics of US catchments, *Hydrological Processes*, 23, 13, 1844-1864.

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Palmer, A.N. (2007), Variations in rates of karst processes, *Acta Carsologica*, 36, 1, 15-24.

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Conclusions

At most sites, SI is correlated to discharge, such that higher discharges result in more aggressive water and higher dissolution rates. The strength of this relationship is strongly correlated to the extent of autogenic versus allogenic recharge, with allogenic settings showing much higher correlations between SI and discharge. The nature of SI-discharge relationships is more weakly correlated to lithological setting (eogenetic vs. telogenetic). On average, the eogenetic sites have more aggressive water, more variation in aggresivity, and significantly steeper SI-Q relationships. However, we cannot rule out the possibility that these correlations result from climatic factors, as all of the eogenetic sites are in a warmer setting with a presumably larger influence of biological activity on saturation state.