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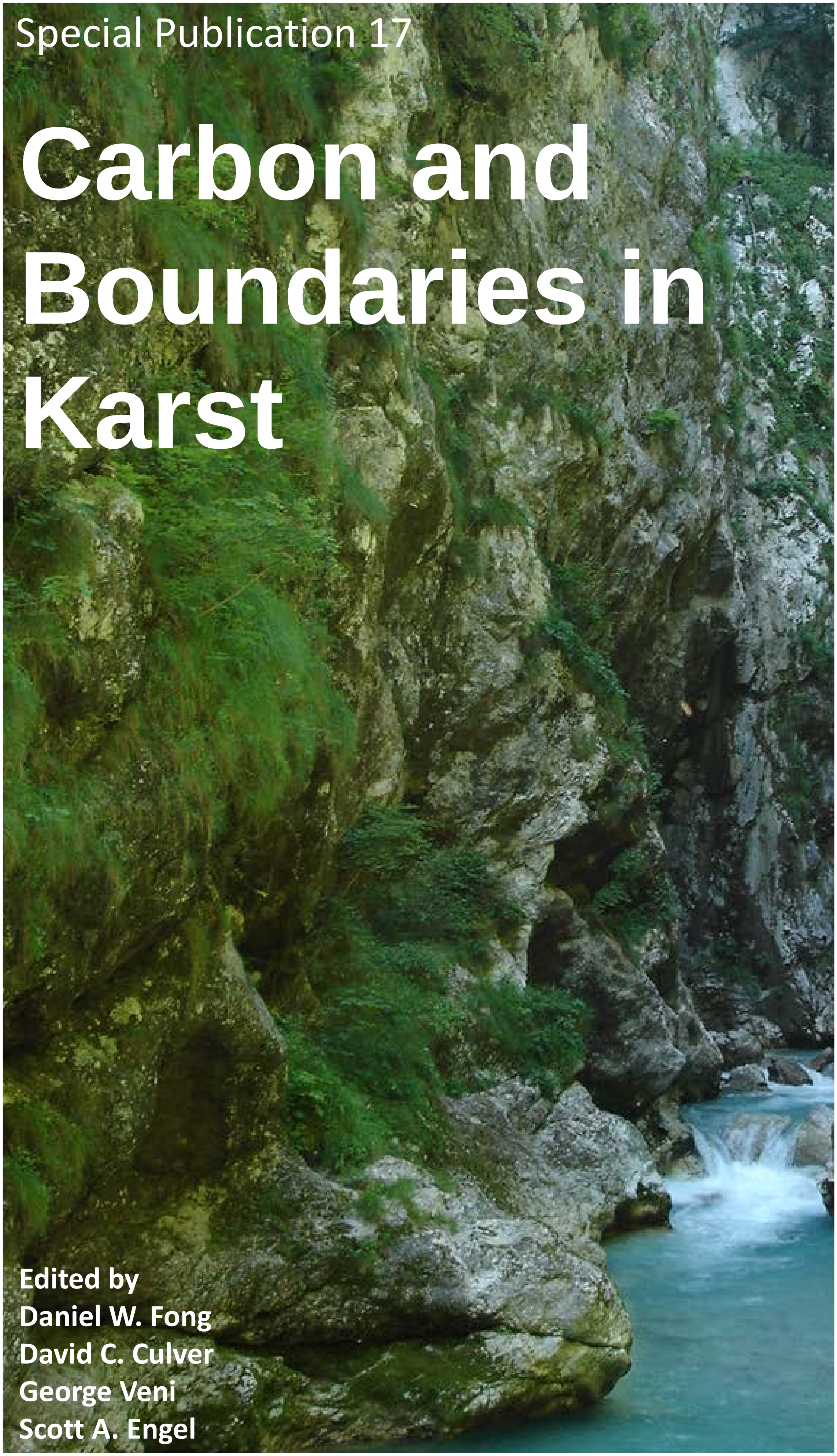

Special Publication 17

Carbon and Boundaries in Karst

Edited by
Daniel W. Fong
David C. Culver
George Veni
Scott A. Engel

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Abstracts of the conference held January 7 through 13, 2013, Carlsbad, New Mexico

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PREFACE

Since the first Karst Waters Institute (KWI) meeting in 1994, KWI Board members have had the following goals for KWI conferences: to build bridges across disciplines, to promote interdisciplinary research, and to provide a forum for the presentation of findings from cutting-edge karst research. The recent KWI conference on ‘Carbon and Boundaries in Karst’ achieved the goals of the organization. The conference balanced technical sessions with a field trip, keynote presentations, and open-ended discussion sessions that provided a forum for the exchange of ideas.

The focus of the meeting was on carbon (organic and inorganic) in karst and the technical sessions were organized to emphasize either a boundary or the processing of carbon: the upper boundary (surface/epikarst), the lower boundary (vadose/phreatic), lateral inputs and outputs, carbon (sources and quality), and microbial processes. For sessions that were organized into boundary zones, the presentations included research designed to advance our understanding of the physical, geochemical, and biological processes involved in the transport, transformation, and storage of various forms of carbon. There were four themes that emerged from the meeting that I would like to highlight.

1) Are there hyporheic zones in karst? The hyporheic zone is a zone (usually associated with a coupled river - alluvial aquifer system) that has a variable thickness and lateral extent, through which surface water and groundwater exchange and mix. The hyporheic zone is a zone of fluid flux, biogeochemical reactions, including processing of organic matter, and the flux of animals. Viewed from the biological perspective, the volume of the hyporheic zone is the depth and lateral extent within which animals, such as stonefly larvae, move. From the fluid dynamics view point, the hyporheic zone can be defined by flowpath segregration patterns from local scale systems that mix with surface water from larger scale systems that do not mix with surface water. Within karst, there are two types of hyporheic zones. One is the porous and cavernous limestone, such as the Floridan aquifer, where groundwater and surface water exchange and mix. The other is the in-cave streambed sediment that acts in a manner similar to a gravel-bedded surface stream. Placing these environments commonly encountered in karst settings in a broader context of ecological and hydrological literature will help to strengthen karst science.

2) Is epikarst a “critical zone”? As defined by the National Science Foundation, a critical zone includes water movement, interactions in the rhizosphere, and interactions with plants. The base of a critical zone is the deepest penetration of roots. There is water movement through the epikarst. Interactions with water-plants and the water-rhizosphere are common in epikarst, as shown by several researchers. Additionally, the epikarst is known for hosting dissolved organic matter in sufficient quantities to support a unique biota that may serve as a staging area for subsequent invasion into the underlying caves. Thinking of studies of epikarst as studies of “the critical zone” is another way to place karst studies within the framework of the larger scientific community.

3) Is the missing carbon sink in the global carbon budgets accounted for by reactions occurring in karst? Most models of the global carbon cycle disregard the role of karst geology, in general, and the role of geochemical reactions that occur in karst, specifically. Weathering of carbonate bedrock that occurs within karst regions of the world is not accounted for in many models of the global carbon cycle, whereas weathering of minerals in silicate bedrock are included. In karst regions of the world, the carbonate reactions are calcite dissolution, tufa formation, and carbonate formation. Some carbonate reactions remove carbon (sink) and other serve as a source of carbon. Regardless of the direction of the reaction, reactions involving carbonate minerals in karst need to be included in models of global change.

4) Can chemoautotrophy support higher trophic levels within cave food webs/chains? Our understanding of the chemoautotrophic reactions, the microbial communities that facilitate those reactions, and the resultant changes in the bulk water composition were well described in the session focused on microbial processes. Evidence of chemoautotrophy has been found even in cave systems that had previously been characterized as hetereotrophic and the notion that chemoautotrophic reactions are unimportant is being reexamined. A question that remains is, “Is the energy (carbon) derived from chemoautotrophic reactions moving to higher trophic levels within the food web?” The innovative use of stream amendments and isotopic tracking are keys to addressing these questions.

In closing, KWI continues to advance karst science and to place karst science within a broader scientific context, whether that context be the hyporheic zone, the critical zone, evolutionary theory, or within a growing subdiscipline (geomicrobiology). In pointing out an obvious achievement of KWI, the field of biogeochemistry in karst systems is now well developed and owes its origins (at least in part) to KWI as the host of the first Geomicrobiology Conference in 1994 in Colorado Springs Colorado USA.

Carol Wicks
Louisiana State University
January 2013

CHEMOTROPHY MEETS HETEROTROPHY: THE INVERTED 'CRITICAL ZONE' OF THE SUBSURFACE

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In Earth's subsurface, a host of poorly known microorganisms conduct their affairs in a dark world typically under extreme energy limitation, both organic and inorganic. This is often accompanied by extreme temperatures, pressures, or highly reactive gases. Are these organisms just evolution's "losers" who have retreated to the subsurface because they simply can't compete for the delicious surface organics? Or are they part of a subterranean microbial biosphere that has persisted over much of Earth's history and may even have originated there? Such a notion suggests an inversion of the ecological concept of a "critical zone" as it is usually applied to surface systems.

Studies of natural caves, both shallow (a few meters) and deep (>1-2 km), and in mines (some >4 km deep) may provide hints about the nutritional and evolutionary status of subsurface microbiota. Although subsurface microbial environments are frequently lumped together, they span a tremendous range of different environmental conditions, just as surface habitats do. Are there systematic differences in microbial biodiversity, nutritional strategy, and other properties with depth that may be distinguishable between shallow, mid-range, and deep crustal levels? While it is still early days, predictions can be made and tested as we continue to explore the depths. We predict a decreasing tendency to heterotrophy and an increasing tendency to chemoautotrophy with depth. This is likely to be accompanied by a depth-dependent decrease in total biodiversity as a result of increasing temperatures resulting from the geothermal gradient, spatial restrictions with only tiny rock fracture spaces available at great depth, but increasing niche richness with increasing macroporosity (aka "caves"!), and limitations in transport mechanisms to move nutrients through the system. We anticipate a biodiversity "sweet spot" where heterotrophic and chemotrophic metabolisms optimally overlap.

Comparative analyses of subsurface geomicrobial lifestyles may provide biomarker proxies for long timescale geological connections, plate motions, and fluid flowpaths, and perhaps offer insights into the origin and early evolution of life.

MICROBIAL CONTROLS ON IN SITU PRODUCTION OF DISSOLVED ORGANIC MATTER

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In most natural systems, microorganisms are responsible for the production and cycling of dissolved organic matter (DOM), despite limited understanding of the roles of microbes in producing DOM. Differences in fluorescence and ultraviolet-visible spectral properties of chromophoric dissolved organic matter (CDOM) were investigated along a 2 km flowpath associated with the Cascade Cave system in Kentucky to understand the relative contributions of microbes in transforming specific allochthonous and autochthonous DOM fractions. Nearly all of the CDOM in the upstream segments of the cave system was determined to be allochthonous, comprised of humic-like DOM contributions consistent with soil or other surface sources. Contributions of autochthonous DOM increased downstream, characterized by the appearance of intense fluorescence spectral peaks attributed to amino acids sourced from microbial activities. It is unlikely that changes in DOM types downstream could be due to enhanced photodegradation, as much of the flowpath was in cave passages, and it is also unlikely that the protein-like fluorescence signatures are derived from wastewater contamination. To interrogate the potential abiotic and biotic controls on DOM transformations along the flowpath, separate microbiological batch experiments using standard DOM compounds and allogenic water before the cave system and resurgence cave water were conducted. Changes to the experimental CDOM were evaluated using several fluorescence indices (e.g., Humification Index, Biological Index, and Fluorescence Index). The relative contribution of new autochthonous DOM increased over time with the addition of either protein-like or humic acid-like reference compounds compared to abiotic controls where no new autochthonous DOM was produced. Combined, these results suggest that microbes in the cave stream were actively transforming the allochthonous DOM into different compounds, and that specific microbial communities along the flowpath were abundant where optimal DOM contributions existed for their metabolism.

REDOX STATE IN KARST AQUIFERS: IMPACTS OF DOC- AND DO-RICH RIVER WATER INTRUSION INTO FLORIDAN AQUIFER SPRINGS

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Focused recharge of surface water into karst aquifers is known to change water chemistry. For example when springs reverse as river stage rises above groundwater heads, river water enriched in dissolved oxygen (DO), dissolved organic carbon (DOC), and trace metals infiltrates the aquifer through the spring vent. The magnitude of changes in the groundwater chemical composition after intrusions is a function of the chemistry of the intruding water, as well as fluxes and residence times of flood waters in the aquifer system. Chemical changes were found to differ following flooding of two springs which discharge from the Floridan aquifer system. The first flood was in March at Madison Blue Spring, which discharges 21°C water to the Withlacoochee River at base flow. During the flood, cold river water (15°C) intruded into the conduit system. The second flood was in July at Peacock Springs, which is connected to the Suwannee River only at high water levels. During this flood, warm river water (28°C) flowed into the conduit system. At both spring systems river water completely displaced groundwater in the conduit system for 8 days and had DOC and DO concentrations above normal spring values (<2 mg-C/L DOC; 1.5-2 mg-DO/L). Intruding water at Madison Blue Spring had lower DOC and more DO (up to 21 mg-C/L; 6.8 mg-DO/L) than at Peacock Springs (up to 48 mg C/L; 3.6 mg/L DO). At both locations groundwater became more reducing when inflow ceased; however, Peacock Springs became more reducing with negative Eh values and mobilization of iron (II) in the system. The greater magnitude of changes during temporary recharge at Peacock Springs was likely influenced both by the chemistry of the incoming water and the local hydrology of the site which increased the length of time the reactive river water was present in the aquifer.

COMPONENT ISOLATION AND LIPID PROFILING TO CHARACTERIZE DISSOLVED ORGANIC MATTER TRANSFORMATIONS ALONG A GROUNDWATER FLOW PATH

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Dissolved organic matter (DOM) is a highly reactive mixture of compounds comprising the majority of organic carbon in aquatic ecosystems. In groundwater, the DOM pool constitutes a fundamental but poorly-constrained element of the carbon cycle. Groundwater-dependent ecosystems, including many karst aquifers, receive seasonal inputs of labile terrigenous organic matter, which is degraded or sorbed over short distances. In deep aquifers, groundwater exhibits unique fluorescence signatures indicative of autochthonous (i.e. in situ) DOM that reflect abiotic processes and nutrient cycling between microbial communities.

To examine the composition and transformation of organic matter in groundwater, we reduced the complex DOM mixtures to recognizable macromolecular groups using diethylamino-ethyl (DEAE) cellulose anion exchange columns. The hydrophilic fraction of DOM was isolated from a cave stream (Cascade Caverns, Kentucky) and two natural organic matter standards (NOM). Two to four liters of water were siphoned onto the DEAE columns to minimize sample aeration. Columns were loaded in the darkness of the cave, or protected from light in the laboratory, to avoid photodegradation. Different eluents, 0.1 M NaOH and 0.1 M phosphate-buffered NaCl, were compared to test for pH effects on macromolecule recovery and preservation.

Organic carbon concentrations in the surface-fed cave stream varied seasonally, ranging from 3.25 mg/L near the swallet to 1.35 mg/L at the spring resurgence 2 km downstream. Organic carbon concentrations in the standards were 0.61 mg/L for Suwannee River NOM and 0.44 mg/L in Nordic Lake NOM. The DEAE columns retained approximately 70% of the DOM measured as organic carbon.

Phospholipid fatty acid (PLFA) analysis was performed on the DOM isolates as a culture-independent technique for quantitatively estimating microbial biomass and characterizing community structure. PLFA were solvent extracted using a modified Bligh and Dyer procedure, fractionated by silicic acid column chromatography, and the polar fraction was derivatized for gas chromatograph-mass spectrometry (GC-MS) analysis.

USING BIOMINERALS TO ASSESS ANTHROPOGENIC INPACT: A CASE STUDY IN CARTER SALT PETER CAVE, CARTER COUNTY, TN

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Anthropogenic impact and eutrophication is a pervasive problem in many caves in the southern Appalachians. Eutrophication can be difficult to visually assess directly in the field, but changes in function among Mn and Fe oxidizing microbial communities are easily seen via changes in the abundance of metal oxide produced.

Carter Salt Peter Cave in eastern Tennessee exhibits Mn(III/IV) oxide formation in biofilms associated with several groundwater seeps as well as on cave litter. Culturing and molecular data indicates that Mn oxide production in groundwater seeps is primarily associated with Mn(II) oxidizing bacteria, while those on cave litter are primarily associated with Mn(II) oxidizing fungi. In 2008, one of the Mn oxide-rich seeps bloomed in a massive Mn oxide biofilm, anecdotally related to a release of sewage in a nearby sinkhole. Molecular methods (16S rRNA) confirmed the presence of Bacteroides-Prevotella human fecal indicators in this seep, and most probable number (MPN) assays and water chemistry confirmed nutrient loading at the site. In both 2009 and 2011, phylogenetic analysis from clone sequences suggested a human-specific fecal signature (with 20-50% of the sequences clustering with human feces sequences). During this time, the seep exhibited a dramatic visual reduction in Mn oxide production, which is hypothesized to correlate with a decrease in nutrient input. MPN analyses suggested that Mn oxidation at the seep was correlated with heterotrophic activity (most likely due to reactive oxygen species production) due to point source exogenous nutrient loading.

Preliminary phylogenetic analysis (using SSU, LSU, and ITS rRNA) to identify Mn(II) oxidizing fungi associated with cave litter revealed the presence of Plectosphaerellaceae sp. DCIF (growing on battery), and two Genus incertae sedis (Fungal sp. YECT1, and Fungal sp. YECT 3, growing on electrical tape) that are are not closely related to any known Mn oxidizing species.

A SIMPLE THEORETICAL FRAMEWORK TO INTERPRET SPRING VARIATIONS AND CONSTRAIN MECHANISTIC MODELS OF KARST PROCESSES

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Prior work on understanding changes in discharge and water quality parameters at karst springs has largely taken two approaches. First, many studies have used statistical analysis or black box models in order to characterize or predict the changes at a spring. This approach has the advantage that it is easy to apply to field data and may allow prediction of spring responses given limited information about aquifer structure. However, it is often difficult to make explicit connections between such analysis and the physical processes occurring within the karst aquifer. Consequently, the other main approach taken has been to construct numerical simulations of the processes that control spring responses. Such models allow direct study of the physics and chemistry that lead to variations at springs. However, these models also suffer from a key weakness. Typically, such studies are limited to a few example cases, and results are difficult to generalize or apply to field sites. Here, we develop a new approach, using simple analytical models of karst flow and transport processes as a tool for interpreting spring variations within a physical framework. These models lead to characteristic time scales and length scales that provide explicit connections between karst conduit geometry and the amplitude of variations in various signals. Ultimately, these simple models provide a bridge between the physics and chemistry realm of the process-based simulations and the statistical and black box approaches. However, potential applications of these models go beyond the study of spring signals. Characteristic length scales can be used to describe many karst processes, often resulting from the boundary between the surface and subsurface. Consequently, these models have implications in a wide range of karst process studies in fields such as hydroecology and geomorphology.

CONVERGENCE AND DIVERGENCE IN CAVES AND SHALLOW SUBTERRANEAN HABITATS

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The dominant neo-Darwinian paradigm of the evolution of cave animals is that the severe aphotic, low food environment with little environmental cyclicity imposes strong selective pressures leading to a convergent (troglomorphic) morphology of reduced pigment and eyes, and elaborated extra-optic sensory structures. Challenges to the paradigm come from two fronts. First, troglomorphic animals occur in many aphotic habitats with relatively abundant food and environmental cyclicity. Second, many permanent reproducing populations in caves are not troglomorphic. A review of data on patterns of troglomorphy confirms both of these points. This suggests that absence of light, rather than resource level and environmental cyclicity, is the important selective factor, and that other forces are at work, including competition and differences in age of lineages in subterranean environments.

THE ROLE OF GEOLOGICAL PROCESSES IN GLOBAL CARBON CYCLE: A REVIEW

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Karst process is a part of geological processes. So it is pertinent to review the history of people's understanding on the carbon cycle in geological processes. Especially to find out why it is sometimes ignored, and being paid more attentions in recent years

The discussions on the relationship between global climate change and the increase of atmospheric green house gas concentration have attracted people's attention on the carbon cycle in the Earth's System. The latter is defined as the processes of the transformation and movement of the carbon between the lithosphere, the hydrosphere, the atmosphere and the biosphere in the forms of CO_3 (mainly $CaCO_3$,$MgCO_3$), HCO_3, CO_2, CH_4, and $(CH_2O)n$ (organic carbon). It can, on the one hand, constrain a series of resources and environmental problems, such as the agricultural, forestry, and cement production, the formation, distribution and burning of fossil fuels, and the change of atmospheric CO_2 concentration, but on the other hand, it is also controlled by a series of geological processes, such as weathering, transport and sedimentation, earthquakes and volcanism. A better understanding on the rules and mechanisms of global carbon cycle is an important scientific reinforcement for sustainable development.

Since knowing the CO_2 in the 17th century, and the discovery of the photosynthesis processes in 1799, human being's exploration on the knowledge about carbon cycle in the earth system has been continuous for about 400 years. In 1896, S. Arrhenius (1859-1927), a Swedish chemist , calculated out on the bases of in situ infrared radiation measurement at different parts of the earth with varied CO_2 and water vapor concentration, that when the atmospheric CO_2 concentration is doubled, the mean air temperature of the earth's surface will rise up 5-6°C; and when the atmospheric CO_2 is reduced to half, the latter will be down 4°C; moreover, if the atmospheric CO_2 concentration is zero, then the mean air temperature of the earth's surface will be down 20°C. A hundred years ago, T. C. Chamberland (1843-1928), an American geologist put forward a hypothesis for the regulation of atmospheric CO_2 concentration by the interactions between exogenic and endogenic geological processes, which include Crust's uplift followed by consumption of more CO_2 from the atmosphere by intensification of weathering processes; the release of CO_2 into the atmosphere by volcanism and deposition of carbonate rocks in the sea; the consumption of CO_2 from the atmosphere by fossil fuel deposition. Chamberlin considered such interactions are responsible for the alternations of warm and cold periods in the earth's history, thus explained the onsets and retreats of the Permian and Quaternary glaciations. But Chamberlin's hypothesis was ignored because of the general acceptance of the contemporaneous (1920) M. Milankovitch's cyclic theory which considered the cold and warm cycles on the Earth's surface are mainly the results of variations in the Earth's orbital parameters. However, in the past couple of decades, the resolution of the past climatic change data has been improved remarkably as a result of the adoption of many new research technologies. People find the Milankovitch cycles cannot explain all the processes behind the periodical changes of the climate, thus shift their attention to the Arrhenius effects, and the impact of geological processes on the global carbon cycle.Twenty-five years ago, the International Geosphere-Biosphere Programme (IGBP) initiated at ICSU (International Council for Science) noticed the carbon cycle in the terrestrial ecosystem, the atmospheric system, and the marine system, thus corresponding multilateral major cooperative projects were put into implementation, including the Global Change and Terrestrial Ecosystems (GCTE), the International Global Atmospheric Chemistry Project (IGAC), and the Land-Ocean Interactions in the Coastal Zone (LOICZ), a lot of scientific progress were achieved. However, the geological processes in the global carbon cycle were ignored because of the limitation of the then carbon cycle model, which took the geological processes as a pure inorganic processes, and their reaction rate are 1-2 order of magnitude less than the carbon cycle in the biological systems. Moreover, the stability of carbon sink in the geological processes was also questioned. In 1995, at the IGBP Scientific Board meeting, the writer made a suggestion to enhance the research on the carbon cycle in the geological processes. Although the suggestion was included in the recommendation of the meeting's resolution, but no substantial step was followed up in IGBP.

In recent years, the fundamental and interdisciplinary researches on carbon cycle in the geological processes have made exciting progress. People find the catalytic function of microbial, especially the *Carbonic Anhydrase* (CA) can make the dissolution rate of CO_2 in the water one order of magnitude higher; it is also found that the photosynthesis process of aquatic algae, and the catalysis of *peptides* on the carbonate deposition can solidify the carbon that enters the hydrosphere. All these discoveries have put a way out for the 2 main puzzles that question the importance of geological processes in the global carbon cycle, i.e., the reaction rate and the stability. Following this trend, the ideas of carbon cycle in the Earth System Science will be improved; the carbon cycle model that knocked together inorganic and organic processes will give way to a more unified reaction process. That will finally renew the carbon cycle model. The international carbon cycle community has enhanced the researches on the geological processes in global carbon cycle. A lot of relevant papers have been published. In China, the National Natural Science Foundation of China (NNSFC), the Ministry of Science and Technology (MOST), and the Ministry of Land and Resources (MLR) have all increased funding in this direction. Investigations, survey, and researches of relevance have been carried out. A monitoring network on the geological processes of carbon cycle that covers all this country is on the way. New data, new discoveries, and new assessment are accumulating. A lot of papers that discuss the carbon cycling in karst processes, in the weathering of silicate rocks, the carbon sink in soil, and CO_2 outgassing from active tectonic zones have been published. Among them, the evidences of enhancing carbon sink in southwest China's karst rock desertification rehabilitation areas could provide scientific background for some climate change mitigation measures in China.

MICROBIAL ACTIVITIES AT GEOCHEMICAL INTERFACES IN CAVE AND KARST ENVIRONMENTS

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Geochemical interfaces at the air-water, water-rock, and air-rock transitions are colonized by microorganisms that influence and control low-temperature geochemical processes like mineral precipitation and dissolution, organic matter transformations and reactions, and metal and contaminant speciation and transport in cave and karst settings. Understanding the effects of microbial processing at geochemical interfaces in cave and karst environments can be done from evaluating microbial diversity and metabolic activities from different types of caves, and conducting experiments to test hypotheses related to rock type, fluid availability and composition, the nature and behavior of organic matter, and habitat history. Microbes colonizing air-water geochemical interfaces are affected by the dynamic exchange of organic and inorganic gases, the formation of aerosols, and physical and molecular forces related to surface tension that create air-water surface microlayers based on the gravity of particles and hydrophobicity of cells. Floating mats and biofilms have been of interest in chemolithoautotrophic cave ecosystems, not only because these biofilms serve as food for higher trophic levels, but because the air-water surface microlayers affect gas exchange, particularly oxygen, with bulk fluids and sediments. Stratification of different anaerobic metabolic groups within the microlayers also affects the production of other gases, including hydrogen sulfide and methane. In contrast, biofilm development at air-rock interfaces in gas-filled passages is influenced by water availability, gas exchange, cell hydrophobicity and charge, and the solid surface charge and nutrient content. Air-rock interfaces are important because microbial processes can lead to cave wall corrosion, subaerial sediment formation, and degradation of surfaces, including Paleolithic cave paintings. Microbial colonization of water-rock interfaces in aquatic habitats reflects dynamic feedback processes associate with fluid geochemistry, ion exchange, and metabolic preferences with respect to carbon and other nutrients. These biofilms are ecosystem food sources, but also are hydrophobic barriers to solute diffusion, which changes water-rock reactions.

INTERACTIONS BETWEEN SURFACE AND SUBTERRANEAN AMPHIPODS IN SPRINGS

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Springs are an ecotone, a contact zone between subterranean and surface fauna. Subterranean species are common in springs – yet we know only little in what relationship are springs and their inhabitants. Some of them may be washed out from a larger subterranean population, and lost for this population. By contrast, some specialized subterranean species might enter springs for feeding. Finally, there are species living only in springs, not specialized for cave environment, but may benefit from relatively stable environmental conditions in springs. All these species may interact with each other. Interspecific interactions determine the composition of spring fauna and may indirectly regulate lateral input and output of organic carbon. In past years we systematically investigated a spring region of Kolaški potok (SW Slovenia) where subterranean amphipod *Niphargus timavi* coexists with surface *Gammarus fossarum*. We first showed that both species coexist for a year-round along upper course of the stream, suggesting that neither of them is accidental in this habitat. A subject of the second study was exploration of interspecific interactions. We showed that both species feed on the same food, but differ in habitat preferences. Surface gammarids predominantly live in decaying leaves, whereas niphargids select either gravel or leaves. Laboratory observations suggests that both species may prey upon each other, but also feed on own juveniles. Contrary to expectations, subterranean niphargids are more aggressive predators than surface gammarids; their juveniles evolved avoidance from adult conspecifics. Proximal causes that underlie spatial separation of the two species were the subject of our third study. Laboratory observations imply that niphargids are more sensitive to light than gammarids. Negative phototaxis seems to be rather widespread trait among niphargids and may be a universal determinant that underlies the coexistence of gammarids and niphargids in springs.

PRELIMINARY CARBON SEQUESTRATION AND DENUDATION RATES WITHIN THE KARST OF THE CUMBERLAND PLATEAU, USA

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The flux and sequestration of inorganic carbon in the Earth system are dynamically linked to Earth's climate past and future. Carbonate aquifers, hosting 60% of the world's proven petroleum reservoirs, 40% of known gas reserves, and influencing approximately 25% of the world's drinking water are particularly vital to our understanding of the carbon cycle. Chemical weathering of carbonates via carbonic acid sequesters CO_2 into the aqueous system. Using the reactions of carbonate equilibrium it is possible to utilize geochemical data to estimate the rate of inorganic carbon that is sequestered from the atmosphere and liberated from the carbonate bedrock, and combining these data with the areal exposure of carbonate rocks can provide one approximation of the rate of landscape evolution.

In this paper, monitoring data and water samples collected from the Redmond Creek Karst Aquifer along the margin of the Cumberland Plateau are combined with GIS data on carbonate rock exposure to evaluate the flux of dissolved inorganic carbon within the Kentucky segment of the Upper Cumberland River. Water-level measurements collected every quarter hour are converted to values of discharge using a hydraulic rating curve. A linear relationship between specific conductance measured every quarter hour and bi-monthly values of pH and the concentrations of Calcium, Magnesium, and total Alkalinity allows 'modeled' values of these parameters.

Geochemical modeling using the ionic species and the modeled discharge reveal a flux of 37 kg of bedrock through Redmond Creek during the 32-week-long study of which 88.5% was calcite and 11.5% was dolomite. This translates to a denudation rate of 6.5 mm/ka within the 10 km^2 of carbonate bedrock exposure. More broadly, over the 3,730 km^2 of carbonate exposure within the Upper Cumberland River of Kentucky, nearly 20,000 metric tonnes of CO_2 are annually sequestered through karst processes into the aqueous system.

DETERMINANTS OF MACROINVERTEBRATE DIVERSITY IN KARST SPRINGS OF THE MID-ATLANTIC REGION, USA

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Karst springs are boundaries or ecotones between the subsurface and the surface environments. There is substantial variation in the diversity of macroinvertebrate communities of karst springs. Much research has focused on variations in the physical and chemical properties of the spring water derived from the subterranean environment as correlates of macroinvertebrate diversity. This study shows that species interactions also play a significant role on structuring the macroinvertebrate communities in karst springs. The amphipod crustacean, *Gammarus minus*, is the dominant macroinvertebrate in a series of karst springs in the mid-Atlantic region of the eastern U.S. The body sizes of sexually mature *G. minus* are significantly larger in springs where its fish predator, *Cottus bairdi*, is present than in springs where it is absent, probably resulting from size-selective predation. Species richness and the Shannon and Simpson diversity indices of macroinvertebrates, and especially the relative abundances of the insect orders Ephemeroptera, Plecoptera and Trichoptera, are lower in springs with larger *G. minus* than in springs with smaller *G. minus*. These results suggest that larger *G. minus* are better at competitively excluding other macroinvertebrates than smaller *G. minus*. Thus body size variation of *G. minus* driven by size-selective predation by its fish predator is one important determinant of macroinvertebrate diversity within the hydrogeological context. Future studies on the relative importance of the biological and physical determinants of macroinvertebrate diversity will allow for an assessment of the sharpness of the boundary between the subterranean and surface environments at karst springs.

BICARBONATE WATER CHEMISTRY OF LITTLE LIMESTONE LAKE, A BEAUTIFUL MARL LAKE IN MANITOBA, CANADA

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Broadly defined, `marl lakes` are those accumulating fine-grained bottom sediments that include at least 15% $CaCO_3$. As such, marl lakes are found in a wide range of environments worldwide. The most visually attractive, however, have much higher proportions of $CaCO_3$, with crystallites precipitating in the water to give it a rich and opaque duck-egg blue coloration. From the literature, such lakes are largely limited to recently glaciated carbonate rock terrains. Most are also shallow, with most or all of the water column being in the photic zone.

Little Limestone Lake, (Lat. 53^o 47`N, Long. 99$^o$ 19`W in the province of Manitoba) is the finest example that the author has seen. Located immediately NW of the northern end of Lake Winnipeg, it stands out sharply from the many neighboring lakes in summertime color satellite imagery due to the intensity and uniformity of its duck-egg blue color. The lake occupies a shallow glacial trough with local relief of 20-25 m that is scoured in a plain of flat-lying cyclothem dolomites.. It is ~12 km in length, 1-5 km wide, rarely >7 m deep. Including bordering wetlands, it occupies ~40% of the area of an elongated, narrow topographic basin. Recharge is through impoverished boreal forest with little soil cover; it discharges chiefly as springs and seeps along the shore. Mean annual temperature is ~0^o C, and precipitation is ~475 mm/yr.

Prior studies of springs in the surrounding region showed the ground waters to be of simple bicarbonate composition, with TDS = 230-300 mg/L (Ca 40-60 mg/L, Mg 30-40 mg/L). The author's grab sampling at 26 sites throughout the lake found the waters degassed to 120-200 mg/L, placing them in the mid-range of one hundred marl lakes investigated in more detail in the British Isles. Ca was reduced to 25-30 mg/L, while Mg was stable at 30-40 mg/L. There were 2-3 Mg/L of free CO_3 in two fully analyzed samples, indicating that some plankton photosynthesis was occurring. However, samples of the bottom marl were predominantly inorganic in their composition.

Little Limestone Lake is visually spectacular because it is almost entirely groundwater-fed, with a ratio of recharge area to lake area that is low. It has no large, chemically equilibrated, surface streams entering it. In contrast, the dozens of nearby lakes (similar, larger or smaller in size) are regularly flushed by channelled storm water and, although they also produce some carbonate marl, cannot maintain high densities of crystallites in suspension. Little Limestone Lake was placed under legislated protection as a provincial park in June 2011.

DYNAMICS AND LIMITATIONS OF ORGANIC CARBON TURNOVER IN POROUS AQUIFERS

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The turnover of organic carbon in porous aquifers is governed by a number of abiotic and biotic processes. In pristine aquifers, it is the low concentration (flux) of DOC and its limited availability and degradability. Typically only a few µg DOC L^{-1} are considered immediately available for maintenance and growth of heterotrophic bacterial biomass. Doubling times of suspended communities are in the range of weeks to years. However, most of the bacterial biomass is found attached to sediment particles, and sediments contain ≥ 1g OM kg^{-1} dw (0.1%), three orders of magnitude more organic carbon than is dissolved in groundwater. In organically contaminated systems biodegradation is controlled by the restricted hydrodynamic mixing, i.e. longitudinal and transverse dispersion, bringing e-donors and e-acceptors together. Sediment heterogeneity is a key driver of mixing and therefore can substantially improve biodegradation. Recently, transient hydraulic conditions were demonstrated to trigger unexpected temporal dynamics of redox processes, a transient collapse of biodegradation activity, as well as profound rearrangements within plume microbiota and contaminant degraders. This presentation will provide a closer look at controls of carbon turnover in pristine and contaminated porous groundwater ecosystems, creating a link to the ecological concept of carrying capacity and seed banks as well as disturbance ecology.

THE LONGITUDINAL RESPONSE OF BENTHIC INVERTEBRATE COMMUNITIES TO CAVES

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Shallow cave systems feed by surface water streams are liable to receive important energy subsidies from the surface. In these systems the cave entrance is a strong ecotonal boundary where resources transition rapidly, and we would expect a marked response of cave invertebrate communities. We investigated the change in resources which occurred at this transition zone in three surface stream-fed caves in Waitomo in the Central North Island of New Zealand. Caves were sampled in austral summer (February-March) during baseflow conditions. On each stream system a total of 12 sites were sampled longitudinally along the stream continuum. Of these, four sites (+128m, +32m, +8m, +4m) were upstream and outside the cave, one at the cave entrance (0m) and seven (-2m, -4m, -8m, -16m, -32m,-128m, -256m) inside the cave. A range of physical, chemical and biological parameters were measured including; light intensity, discharge, water chemistry, physical in-stream habitat, aquatic and terrestrial invertebrates. Loggers measured wind-run, air and water temperature for the duration of study. Not surprisingly marked changes occurred in several physico-chemical parameters (e.g., light intensity, air temperature). Algal biomass (chlorophyll a) decreased as light levels declined, and CPOM biomass also significantly declined along the gradient. Stream invertebrate taxonomic richness and density fluctuated at the cave mouths but decreased from the cave entrance into the cave. Aquatic adult emergence was greatly reduced inside the cave, however stable isotope analysis of cave terrestrial invertebrate predators (e.g. glow-worms, spiders and harvestmen) showed a strong dependence of aquatic prey. Our results indicate that upstream subsidies play an important role in maintaining cave foodwebs in these shallow cave systems. Thus, changes in surface land use activities can have unforeseen consequences on the ecology of associated, recipient cave systems.

EXPERIMENTAL DESIGN AND INSTRUMENTATION TO OBSERVE KARST CONDUIT HYPORHIEC FLOW

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We are finalizing plans for a field project to observe pressure driven conduit-matrix exchanges at the margin of phreatic conduits in eogenetic karst. The primary exchange of investigation is analogous to hyporheic flow in surface streams. Thus, we call our targeted exchange "karst conduit hyporheic flow". As with surface streams we expect this exchange will play a role in redox cycling, contaminant transformation, and a variety of biogeochemical reactions.

Our plan to observe karst conduit hyporheic flow requires sampling from narrow boreholes drilled (< 1m) into the matrix from the conduit wall. This will require underwater coring and placing a multilevel water sampler in the core holes. We have developed both sets of hardware for this application.

A reviewer of our field project test called it "some of the most delicate work I've seen proposed". We would like to improve our designs and are actively soliciting comments and suggestions. In this poster we outline the evolving experimental plan, and show our computational fluid dynamics models, which we use to guide our experimental design. We detail the design of underwater coring devices and the multilevel water sampler which has permeable packers. We present our guiding computational fluid dynamics models and detail our sampling and analysis plan.

BIOLOGICAL CONTROL ON ACID GENERATION AT THE CONDUIT-BEDROCK BOUNDARY IN SUBMERGED CAVES

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No-Mount Cave, located in Wekiwa Springs State Park in central Florida, is an aphotic, submerged, freshwater cave in which large colonies of sulfur-oxidizing bacteria live in filamentous microbial mats. Upwardly discharging groundwater enters the cave from the Upper Floridan Aquifer, specifically the Eocene-aged Ocala Limestone. We undertook a combined field, laboratory, and modeling study in which we sought to determine the amount of calcite dissolution attributable to the generation of protons via microbially mediated sulfide oxidation. Using information on the chemical composition of groundwater within the limestone formation and within the cave conduit, we used the reaction-path model PHREEQCI in order to quantify the amount of calcite dissolution possible due to bacterial sulfide oxidation. Literature-based assumptions about energy yield for biomass production from sulfide oxidation were incorporated into the modeling effort, while the extent and rate of microbial growth in this context are currently under study in our laboratory. Using a mass balance on biomass production and on the transformation of the aqueous sulfur species, the modeling results indicated a maximum amount of 230 mg Ca^{2+} released to conduit water per liter of groundwater crossing the formation-conduit boundary, simulating the extent of calcite dissolution. Analogous laboratory experiments were conducted using flow-through columns packed with crushed limestone from the site. Replicate columns were eluted with artificial groundwater containing dissolved H_2S in the absence of microbial growth. No measurable calcite dissolution occurred, but abiotic sulfide oxidation under the experimental conditions of flow rate and residence time was also minimal. Our modeling results indicate that significant cave development under these hydrogeochemical conditions depends upon microbially mediated sulfide oxidation as a source of acid.

ENVIRONMENTAL CONTROLS ON ORGANIC MATTER PRODUCTION AND TRANSPORT ACROSS SURFACE-SUBSURFACE AND GEOCHEMICAL BOUNDARIES IN THE EDWARDS AQUIFER, TEXAS, USA

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Karst aquifer phreatic zones are oligotrophic habitats supported by organic matter (OM) flow across physical and geochemical boundaries. Photosynthetic OM enters the Edwards Aquifer of South-Central Texas via streams sinking along its northeastern border. A rapid transition between oxygenated freshwaters and anoxic saline waters marks the southeastern boundary where OM is produced by chemolithoautotrophic microbes. Spatial and temporal heterogeneity in OM composition at these boundaries was investigated using isotopic and geochemical analyses. $\delta^{13}C$ values for fine particulate OM (FPOM) (-11.47‰ to -33.34‰) decreased during regional drought between fall 2010 and spring 2012 ($t=5.02$, $df=16$, $p<0.01$), and $\delta^{13}C$-FPOM in streams and recharge zone groundwater sites were correlated with C:N ratios (quantile regression $\tau = 0.9, 0.75, \& 0.5$, $p<0.01$), possibly due to decreased terrestrial plant contribution, increased relative periphyton contribution, and greater microbial processing. Average δ13C composition of stream FPOM transported into the aquifer, weighted by discharge, was estimated at δ13C-FPOM=-21.75‰. Along the freshwater-saline water interface (FWSWI), $\delta^{13}C\text{-}FPOM_{fwswi}$ (-7.23‰ to -58.18‰) became enriched through time ($t=8.65$, $df=10$, $p<0.001$) and was positively correlated with dissolved inorganic carbon (DIC) $\delta^{13}C$ values (-0.55‰ to -7.91‰) ($F=18.32$, $df=1 \& 22$, $p<0.01$). $\delta^{13}C$-DIC ($F=35.15$, $df=1 \& 26$, $p<0.01$) and $\delta^{13}C\text{-}FPOM_{fwswi}$ ($F=13.61$, $df=1 \& 26$, $p<0.01$) were correlated with longitude. Reasons for the temporal trend in $\delta^{13}C\text{-}FPOM_{fwswi}$ may be due to environmentally driven recharge and aquifer level changes affecting transport of chemolithoautotrophic OM across the FWSWI. $\delta^{13}C\text{-}FPOM_{fwswi}$ was depleted relative to $\delta^{13}C$-DIC by 29‰: within the range of fractionation factors reported for carbon fixation by RubisCO, and correlation between $\delta^{13}C$-DIC and $\delta^{13}C\text{-}FPOM_{fwswi}$ suggests that DIC is a substrate for chemolithoautotrophic production at the aquifer scale. Spatial variability in $\delta^{13}C$-DIC is likely due to local differences in the relative proportions of young and old waters, mixing with brines containing CH_4, and variable sources of acidity driving carbonate dissolution.

CARBON AND CO_2 IN THE PHREATIC/EPIPHREATIC ZONE OF KARST SYSTEMS. SOME IDEAS, DATA AND QUESTIONS FROM THE MILANDRE KARST LABORATORY (SWITZERLAND)

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Observations along the last 22 years in Milandre karst system evidenced a significant increase (about 10%) in water hardness at the spring of the system (Fig. 1). This observation is validated by similar observations in 15 karst systems of the same region.

One possible explanation to this evolution is that temperature increase observed in the catchment area, induced an increase of the CO_2 production in the soils, and then an increase of the CO_2 concentration in the vadose zone of the system (cave) leading to a higher pCO_2 at the top of the phreatic zone, then to higher hardness values. Another explanation is that the flux of organic carbone in the water increased along this period of time (soil erosion) leading much sediment and biological activity in the cave-system. The storage of sediment is significant in the epiphreatic zone (and possibly in the phreatic zone as well) and a significant biodegradation could be observed. High CO_2 concentrations are correlated to periods of high biodegradation activity. This could thus also be a reason for the observed increase in water hardness.

The Milandre karst laboratory provides data on CO_2 productions, sedimentation and water characteristics at various locations within the karst system. Together with data from the literature, it will be used to sketch general concepts and suggest experiments as well as monitoring for improving our understanding of carbon in karst systems.

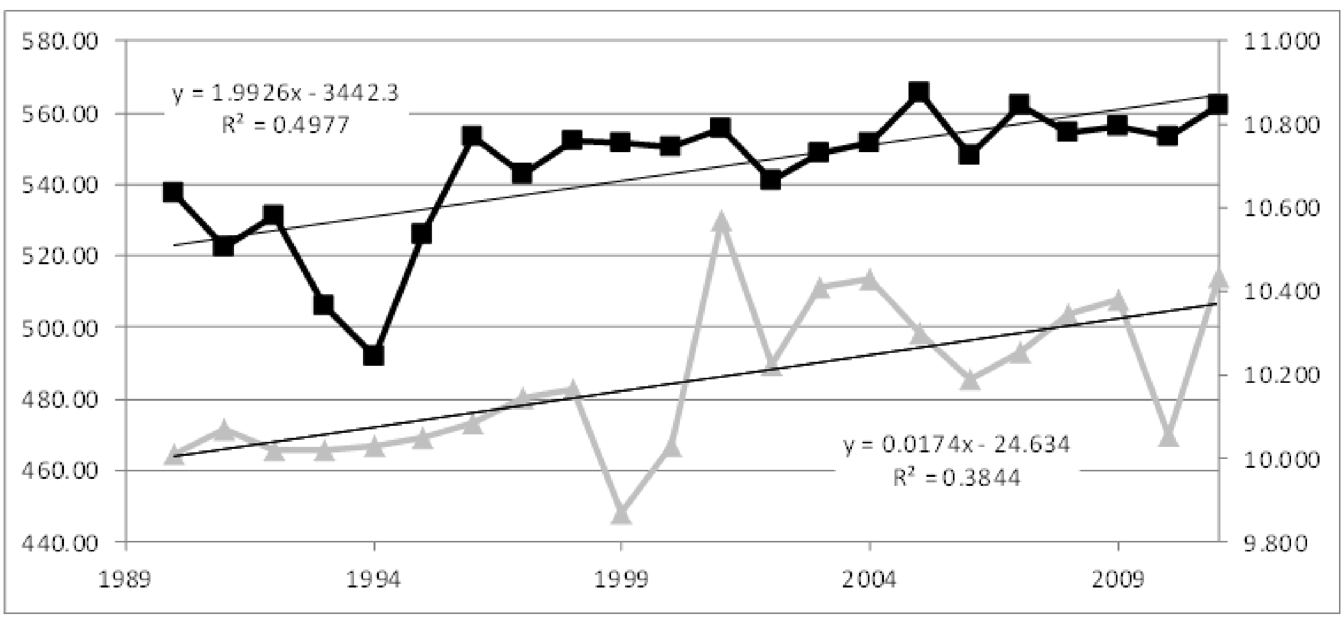

Figure 1: Evolution of water electrical conductivity (black curve, left axis in µS/cm at 20°C) and of water temperature (grey curve, right axis in °C) in Milandre cave stream. Dots are annual mean values from 15 minutes measurements.

SUBAERIAL MICROBIAL LIFE IN THE SULFIDIC FRASASSI CAVE SYSTEM, ITALY

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The sulfidic Frasassi cave system, Italy, hosts a subterranean chemotrophic ecosystem that includes numerous endemic invertebrates and diverse microbial life. At the cave water table, $H_2S(g)$ flux from sulfidic springs provides energy for sulfide-oxidizing microbial communities that colonize cave walls and ceilings. On exposed limestone surfaces, mildly acidic (pH 6) microbial communities inhabit anastomosing organic-rich sediments known as biovermiculations. Based on stable isotope ratios of C and N, the organic material in Frasassi biovermiculations derives from the sulfidic cave ecosystem rather than from surface sources, and molecular analyses indicate the presence of possible sulfur-oxidizing taxa. Biovermiculation formation is most rapid in sulfidic cave zones, although they occur over extensive areas where no $H_2S(g)$ is detectable. However, biovermulations are rare in immediate proximity to sulfidic springs, likely due to the formation of gypsum wall crusts. Gypsum crusts form as corrosion residues and provide a substrate for extremely acidic (pH 0-1) biofilms known as 'snottites.' Molecular and metagenomic analyses have shown that Frasassi snottites are among the least diverse biological communities known, and are populated by a handful of acidophilic bacterial and archaeal taxa. All snottite communities sampled to date are dominated by sulfur-oxidizing autotrophs of the genus Acidithiobacillus, which are likely responsible for snottite formation. The microbial communities of the gypsum wall crusts themselves are underexplored, although preliminary data indicates that acidic gypsum residues (pH 2) are similar to snottite communities but with lower cell densities and proportionally less Acidithiobacillus. Due to their extreme geochemistry and isolated subsurface location, sulfidic caves are valuable settings for studies that address fundamental questions of microbial ecology and evolution. We report results of one such study in which we used sulfidic cave snottites as natural experiments to test if and how dispersal restrictions and historical effects influence the biogeography of microorganisms.

PHYSICAL STRUCTURE OF THE EPIKARST

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Epikarst is a weathered zone of enhanced porosity on or near the surface or at the soil/bedrock contact of many karst landscapes. The epikarst is essentially the upper boundary of a karst system but is also a reaction chamber where many organics accumulate and react with the percolating water. The epikarst stores and directs percolating recharge waters to the underlying karst aquifers. Epikarst permeability decreases with depth below the surface. The epikarst may function as a perched aquifer with a saturated zone that transmits water laterally for some distance until it drains slowly through fractures or rapidly at shaft drains or dolines. Stress-release and physical weathering as well as chemical dissolution play a role in epikarst development. Epikarst may be found on freshly exposed carbonates although epikarst that develops below a soil cover should form at a faster rate due to increased carbon dioxide produced by vegetation. The accumulation of soil within the fractures may create plugs that retard the downward movement of percolating water and creates a reservoir rich in organic material. The thickness of the epikarst zone typically ranges from a few meters to 15 meters, but vertical weathering of joints may be much deeper and lead to a "stone forest" type of landscape. Some dolines are hydrologically connected directly to the epikarst while other dolines may drain more directly to the deeper conduit aquifer and represent a "hole" in the epikarst. Water stored in the epikarst may be lost to evapotranspiration, move rapidly down vertical shafts or larger joints, or drain out slowly through the soil infillings and small fractures.

SEASONAL, DIURNAL AND STORM-SCALE PCO_2 VARIATIONS OF CAVE STREAM IN SUBTROPICAL KARST AREA, CHONGQING, SW CHINA

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CO_2 in karst have been growing interest since the IGCP 379 project started in 1995. An open question is about the dynamics of carbon in karst systems, and particularly carbon flux between the surface and subsurface and between different components in the karst subsurface. This research specially focuses on the variations of PCO_2 (CO_2 partial pressures) in subtropical karst groundwater, using high−resolution auto-monitoring hydrochemical data (15 min intervals). Our study aim was to understand how PCO_2 in karst systems responds to recharge at different time scales, and further what the controlling factors are. An auto−monitoring station on hydrochemistry was set in the channel of cave stream in Xueyu cave, a typical subtropical karst cave, about 300m away from exit. Four−year high−resolution continuous pH, electrical conductivity (Ec), temperature and water stage of typical cave streams were collected. A thermodynamic model was used to link the continuous data to monthly water quality data allowing the calculation of CO_2 partial pressures and calcite saturation (SIc) levels on a continuous basis. Seasonal, diurnal and strom−scale variations were captured for PCO_2 and calcite saturation indexes of the cave stream, indicating that cave stream are dynamic and variable systems. The seasonal of these features (higher conductivity and lower pH in summer; lower conductivity and higher pH in winter) tend to covary with temperature which influences the production of CO_2 in soils, thus being the driving force for the variations (soil CO_2 effect). Due to the buffer of the thick vadose zone and cave space, the diurnal variation is not obvious compared with other reported epikarst springs in SW China. The storm-scale fluctuations occur during the summer rainy days due to the storm−events. The piston effect, dilution effect and soil CO_2 effect dominate the variations in different storm-events. At the beginning period of rainfall, the piston effect affects the variations, characterized by the increase in Ec, SIc and pH of cave stream and decrease in PCO_2. At heavy rainfall, the decrease in Ec shows the control of dilution effect, while the decrease in SIc and pH and increase in PCO_2 shows the influence of soil CO_2 effect. At lower or medium rainfall intensity, soil CO_2 effect determines the variations, characterized by increase in CO_2 partial pressure and Ec but decrease in pH and SIc. In a word, the hydrodynamic aspects, hydrobiogeochemical characteristics and cave space need to be taken into account to correctly explain the PCO_2 and hydrochemical variations of the subtropic cave stream.

STRATIGRAPHIC CONTROL ON CONDUIT DEVELOPMENT IN THE OZARK KARST, MISSOURI, USA

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It has been recognized that caves and karst conduits in general tend to form at particular, localized stratigraphic positions. The controlling mechanisms for this phenomenon are poorly understood. Conduits in the Upper Cambrian and Lower Ordovician carbonates on the Ozark Plateau in central and south-central Missouri, often form near the top of the formations and below units that are frequently, but not always, sandstone. One possibility is that the conduits form at that stratigraphic position because the overlying sandstone layer acts as an aquitard resulting in increased partial pressure of carbon dioxide and concomitant increased aggressiveness. We propose that conduits are forming along zones of enhanced secondary hydraulic conductivity which occur near the top of shallowing-upward, third order Vail cycles. These zones have significant, extensive stromatolitic layers which have become silicified prior to dolomitization of the carbonate sequence. The silicification process is volume conserving while the dolomitization results in a decrease in volume thus enhancing secondary porosity and hydraulic conductivity. Furthermore, the facies occurring near the top of a shallowing- upward sequence exhibit numerous paraconformities due to subareal exposure and karstification during early diagenesis. These facies have very high vertical to horizontal hydraulic conductivity ratios, allowing for enhanced horizontal fluid flow. Zones of enhanced hydraulic conductivity focus flow through the bedrock and result in facies-dominated karst horizons.

USING ISOTOPES OF DISSOLVED INORGANIC CARBON SPECIES AND WATER TO SEPARATE SOURCES OF RECHARGE IN A CAVE SPRING, NORTHWESTERN ARKANSAS

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At Blowing Spring Cave in northwestern Arkansas stable isotopes of water ($\delta^{18}O$ and δD) and inorganic carbon ($\delta^{13}C$) were used to quantify soil-water, groundwater, and precipitation contributions to cave-spring flow during storm events to understand controls on cave water quality. Gaseous and aqueous phase samples in recharge-zone soils and from the cave were collected from March to May 2012 to implement a multicomponent hydrograph separation approach; samples included gaseous carbon dioxide ($\delta^{13}C$-CO_2), aqueous dissolved inorganic carbon ($\delta^{13}C$-DIC), and $\delta^{18}O$ and δD of water. During baseflow, median δD and $\delta^{18}O$ values were -42.0‰ and -6.2‰ for soil-water and values were 36.9‰ and -5.5‰ for groundwater, respectively. Median DIC concentrations for soil-water and groundwater were 1.8 mg/L and 24.6 mg/L, respectively, and median $\delta^{13}C$-DIC values were -20.0‰ and 14.5‰, respectively. During a March storm event, 12.14 cm of precipitation fell over 82 h and discharge increased from 0.01 to 0.65 m^3/s in 59 h. The isotopic composition of precipitation varied throughout the storm event because of rainout (50‰ and 10‰ for δD and $\delta^{18}O$, respectively); although, at the spring, δD and $\delta^{18}O$ only changed by approximately 3‰ and 1‰, respectively. The isotopic compositions of precipitation and pre-event (i.e., stored) water were isotopically similar and a two-component hydrograph separation either overestimated (>100%) or underestimated (<0%) the contribution from precipitation to the spring. During the storm event, DIC and $\delta^{13}C$-DIC decreased to a minimum of 8.6 mg/L and -16.2‰, respectively. If the contribution from precipitation was assumed to be zero, soil water was found to contribute between 38 to 68% of the total volume of discharge. Although the assumption of negligible contributions from precipitation is unrealistic, especially in karst systems where rapid flow through conduits occurs, the hydrograph separation using inorganic carbon highlights the importance of considering vadose-zone soil-water when analyzing storm chemohydrographs.

QUANTITATIVELY MODELING SOURCE INFLUENCES ON CAVE AIR CARBON DIOXIDE CHEMISTRY

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Long term, near continuous, in-situ monitoring of cave air chemistry in a NW Florida cave from October 2007 to February 2009 allows investigations into the relationship between the $\delta^{13}C$ signature and concentration of cave air CO_2, where these signatures are derived, and the influence of the atmosphere on cave air CO_2. Cave air CO_2 in Hollow Ridge Cave is a simple two end-member mixing system assumed to be conservative over short time periods, with soil gas (lower $\delta^{13}C$, higher CO_2) and atmosphere air (higher $\delta^{13}C$, lower CO_2) as the end-members. A regression analysis of $\delta^{13}CO_2$ versus inverse [CO_2] has a linear relationship similar to that found in atmospheric, soil, and snowpack CO_2. This relationship predicts both the soil and atmospheric end-members, which can be compared to field samples; in this study a predicted soil-gas $\delta^{13}CO_2$ of −22‰ and atmospheric $\delta^{13}CO_2$ of −7‰. (Kowalczk and Froelich, 2010). Atmospheric samples analyzed at 390 ppmv CO_2 and -7.25‰, while soil gas samples analyzed at 3800 ppmv and -20.5‰, suggesting predicted CO_2 values from the regression are accurate. This regression was applied to the continuous CO_2 time-series and modeled cave air $\delta^{13}CO_2$. These data, along with measured $\delta^{13}C$ and CO_2 of soil and atmospheric samples, model the quantitative influence of the atmosphere on cave air CO_2 chemistry. Various locations in the cave show variable atmospheric influence (36 to 98%) to strong stagnation (less than 25%) in the summer, while atmospheric influence in the winter ranges from 50-98%. These relationships could be applied to any cave air CO_2 time series when both end-members are known or accurately estimated. This relationship may assist in determining whether the $\delta^{13}C$ signature of cave air CO_2 or the $\delta^{13}C$ signature of DIC in drip waters is more significant in determining the $\delta^{13}C$ of calcite in deposited speleothems.

QUATERNARY GLACIAL CYCLES: KARST PROCESSES AND THE GLOBAL CO_2 BUDGET

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Extensive research has been conducted looking at the relationship between karst processes, carbonate deposition and the global carbon cycle. However, little work has been done looking into the relationship between glaciations, subsequent sea level changes, and aerially exposed land masses in relation to karstic processes and the global carbon budget. During glaciations sea-level exposed the world's carbonate platforms. With the sub-aerial exposure of the platforms, karst processes can occur, and the dissolution of carbonate material can commence, resulting in the draw down of CO_2 from the atmosphere as HCO_3^-. Furthermore, the material on the platforms is primarily aragonite which is more readily soluble than calcite allowing for karst processes to occur more quickly. During glaciations arctic carbonates and some of the temperate carbonates are blanketed in ice, effectively removing those areas from karst processes. Given the higher solubility of aragonite, and the extent of carbonate platforms exposed during glaciations, this dissolution balances the CO_2 no longer taken up by karst processes at higher latitudes that were covered during the last glacial maximum The balance is within 0.001 GtC / yr, using soil pCO_2 (0.005 GtC / yr using atmospheric pCO_2) which is a difference of about 0.1% of the total amount of CO_2 sequestered in a year by karst processes. Denudation was calculated using the maximum potential dissolution formulas of Gombert (2002). On a year to year basis the net amount of carbon sequestered through karstic processes is equivalent between the last glacial maximum and the present day, however, the earth has spent more time in a glacial configuration during the Quaternary which suggests that there is a net sequestration of carbon during glaciations from karst processes which may serve as a feedback to prolong glacial episodes. This research has significance for understanding the global carbon budget during the Quaternary.

KARST IN THE GLOBAL CARBON CYCLE

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Carbonate minerals contain 6 x 10^7 Gt of carbon or about 3 orders of magnitude more carbon than the oceans, 4 orders of magnitude more than the biosphere or buried fossil fuels, and 5 orders of magnitude more than the atmosphere. Dissolution of $CaCO_3$ by carbonic acid produces two molecules of bicarbonate, one from atmospheric or soil CO_2 and a second from the mineral. Precipitation of $CaCO_3$ releases CO_2 to the atmosphere. These two processes are thought to be balanced over long time periods and at global scales, resulting in zero net flux of atmospheric CO_2. Recent work has proposed burial of organic carbon produced from DIC originating from carbonate mineral dissolution represents a net sink of 0.5 to 0.7 Gt/yr of atmospheric CO_2, thereby impacting the global carbon cycle. The magnitude of this impact depends on linkages between primary productivity, organic carbon, and carbonate mineral dissolution and precipitation. Studies of these linkages in karst streams in north-central Florida show primary productivity controls carbonate mineral saturation states at diel frequencies. In addition, organic carbon discharged from wetlands to these streams is mineralized to CO_2, decreasing pH, and leading to localized dissolution of carbonate rocks. Approximately 10% of the dissolved inorganic carbon evades to the atmosphere, but the remainder discharges as bicarbonate to the ocean. This bicarbonate may precipitate to form modern carbonate platforms, where organic carbon mineralization through sulfate reduction and oxidation of the produced sulfide dissolves carbonate minerals, providing a net source of CO_2 to the atmosphere and limiting burial of carbonate minerals. Carbonate minerals thus represent both short-term local sinks and sources for atmospheric CO_2, which impact local carbon cycling. Processes controlling these local sources and sinks are likely to be balanced over long time scales, thereby limiting their impacts on the global carbon cycle.

SPATIO-TEMPORAL TRENDS IN DIVERSITY OF SUBSURFACE ASSEMBLAGES FROM THE VADOSE ZONE OF THE CARPATHIAN KARST IN ROMANIA

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Recent studies highlighted the importance of the vadose zone as a particular ecosystem sustaining a highly specialized and unique fauna. When caves provide a limited access into the fissures within the vadose zone, samples from pools and drip water are commonly used as an indirect method to assess the biological dynamics of the vadose zone system.

Copepods are the most diversified and abundant, probably the most characteristic taxon roaming the vadose voids of the Romanian Carpathians. The spatial and temporal changes in copepod community composition in relation to the environmental features were studied at local and regional scales.

Canonical Correspondence Analysis was performed to explore the relationships between temporal variation of fauna in pools and drips and a series of environmental parameters over a period of 12 and 7 months respectively. Occurrence of the epigean species underground was influenced by precipitation and the drip rates amount. The occurrence of the hypogean species was related with electrical conductivity, which can be an indicator of the residence time of water in the vadose zone. It is shown that forest cover might be one of the most important driving factor influencing the copepod diversity and abundance.

At regional scale, ArcGIS was used to develop habitat-based modelling in order to predict suitable areas for seven copepod taxa. Six environmental features were selected from freely available sources to serve as model parameters. Ordinary least squares regression and geographically weighted regression were used to identify the significant predictors for explaining copepod habitat suitability. The most constant predictor was land cover, a measure of human impact, followed by precipitation and elevation. Hypogean taxa were the main taxa correlated with land cover.

Both approaches substantiate the important role of sustainable management regarding the surface areas of karst landscape as a priority in protecting and conserving the groundwater resources.

COMPARISON OF WATER CHEMISTRY IN SUBMERGED CAVES WITH THAT OF DIFFUSE GROUNDWATER IMMEDIATELY PROXIMAL TO THE CONDUIT

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Walls of submerged caves feeding Florida springs are often lined with a heavy mat of filamentous bacteria, many of which are able to oxidize reduced sulfur in groundwater migrating from the porous rock into the cave conduit. This oxidation produces sulfuric acid. We posit that that acid production can accelerate the enlargement of the caves in a process we call biospeleogenesis. To determine changes in water chemistry as water passes through the microbial mat, a simple device made from well screen and sealed with a rubber stopper and controllable vents was installed in a hole drilled in the rock. The sampler was sealed in place with marine epoxy. We measured anions in water from the sampler and from the water-filled conduit taken just outside the sampler. Most anions measured, viz., Cl^-, NO_3^-, and PO_4^{3-}, did not differ significantly between the proximal and conduit waters. However, traces of sulfide were measured in the water from the rock, but not in the cave. SO_4^{2-} concentrations in the conduit were about twice that measured in the water from the sampler, about 22 and 11 mg SO_4^{2-} L^{-1}, respectively, suggesting that sulfur oxidation is an important process in the mats attached to the limestone surfaces in these caves possibly resulting in biospeleogenesis. An additional use of the sampling device is to measure discharge from the local bedrock into the cave conduit, thereby supporting mixing calculation for geochemical reaction modeling.

CARBON CYCLING IN ARID-LAND CAVES: IMPLICATIONS FOR MICROBIAL PROCESSES

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Previous work that has been done on carbon cycling in caves has been conducted in karst regions that receive considerable precipitation and with caves that often have streams running through them. Arid-land caves, such as those found in New Mexico, exist under surface conditions that are considered semi-arid and surface moisture infiltrates very slowly into these caves, sometimes taking decades to reach pools hundreds of feet below the surface. We have investigated the levels of organic carbon (and nitrogen and phosphorus) in surface soils above caves and in soils and rock deposits within the underlying caves. Organic carbon levels within the caves varied from 0.1 to 6%, with the highest levels being observed in some of more shallow lava caves or the carbonate cave that floods, and the lowest levels being observed in the deepest carbonate caves (i.e. Lechuguilla Cave in Carlsbad Caverns National Park). However, organic carbon distribution within caves is highly variable. Our studies show that sparse nutrients in caves lead to the production of extracellular enzymes by microorganisms to break down complex nutrients and that extracellular enzyme activities (EEA) are highly variable within and between caves. Our initial studies of the degree to which organic carbon levels correlate with antimicrobial activity observed in cultured isolates, do not show any strong trends. These studies are providing a picture of the organic carbon levels in arid-land caves and the possible implications for microbial inhabitants of these caves. Future efforts will continue to explore the implications of nutrient cycling on microbial communities in arid-land caves, with the eventual goal of being able to compare these with studies done in higher precipitation environments.

SHALLOW SUBTERRANEAN HABITATS IN VOLCANIC TERRAIN

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Volcanic terrains have more abundant, widespread subterranean habitats than expected, often being suitable for adapted fauna. Deep habitats such as caves are found in basaltic pahoehoe lavas and more rarely in other type of rocks, occurring in terrains within a limited rank of geological ages. However, shallow subterranean habitats can originate in a variety of volcanic rocks and structures, and can evolve into different types as time goes on. The mesocavernous shallow substratum (MSS) is very widespread, occupying most of the subsurface areas with the exception of compact, impermeable acidic rocks, such as trachytic or pumitic tuffs. There are three types of MSS: a) that originated by rock meteorisation in early stages of pedogenesis, b) the colluvial MSS formed by scree at the base of cliffs, eventually covered by soil, c) the volcanic MSS structured by the clinker of recent and subrecent lavas covered by soil before being eroded. A particular type of subsurface habitat is that originated by drifts of cinders and lapilli, being occupied by subterranean animals up to a few centimeters below surface.

The pedogenic and colluvial MSS's have originated after long periods of time, are usually found in old terrains currently covered by forest, and have a higher input of organic matter. The volcanic MSS and the cinder fields are geologically much more recent, usually more exposed and with less availability of organic nutrients. The Canary Islands form a volcanic archipelago with seven islands ranking from 22 to 1 million years old, each with a long history of volcanic activity and calm periods, and with a diversity of volcanic rocks. All this has provided a good variety of subsurface habitats which have been occupied by a rich fauna, with different degrees of adaptation according to the age and food richness of the underground.

PARTICULATE INORGANIC CARBON FLUX IN KARST AND ITS SIGNIFICANCE TO KARST DEVELOPMENT AND THE CARBON CYCLE

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Carbonate bedrock weathering has been recognized as a significant component of the global atmospheric carbon sink. Studies of atmospheric carbon sink processes and landscape evolution in carbonate bedrock terrains have focused primarily on dissolved inorganic carbon flux. Particulate inorganic carbon (PIC) in the sediment load of karst waters is frequently dismissed as insignificant for calculating denudation and carbon transport/sink rates, because chemical processes are assumed to greatly dominate. PIC flux from carbonate terrains may be an important missing term in carbon cycle and denudation calculations because carbonate sediment continues to dissolve in undersaturated water downstream of sampling points. The research objective is to quantify PIC transport and loads in karst settings, and determine if PIC can be a significant variable in the karst carbon cycle.

Quantifying PIC loads is being accomplished by measuring sediment load entrainment and transport in karst stream conduits at Mammoth Cave, KY; Blowing Cave, KY; and Tumbling Creek Cave, MO. Bed load flux is being measured by RFID tagging and traps. Automatic samplers and data loggers are used to determine suspended load and water chemistry. The percentage of PIC within sediments is being quantified by x-ray diffraction or differential titration (fine fraction) and visual analysis and separation (coarse fraction). The mixing of new versus reworked suspended sediment in conduits is estimated by quantifying short-lived cosmogenic isotopes. The PIC results will be compared to dissolved inorganic carbon measurements to determine the significance of each component of carbon removal.

PATTERNS OF ORGANIC CARBON IN SHALLOW SUBTERRANEAN HABITATS (SSHS)

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Organic carbon is likely to be a limiting factor in shallow subterranean habitats (SSHs). Data on dissolved organic carbon (DOC) for hypotelminorheic and hyporheic SSHs are reviewed, and compared to nearby streams and springs, all on Nanos Mountain in Slovenia. These results are compared to extensive estimates of organic carbon in epikarst sites in Postojna Planina Cave System (PPCS) in Slovenia and Organ Cave in the U.S.A. The four hypotelminorheic sites showed both spatial and temporal heterogeneity. Median DOC values ranged between 1.1 and 7.0 mg L^{-1}. The most diverse hypotelminorheic habitat had a DOC value of 2.7 mg L^{-1}. Median DOC value for the one hyporheic site was 1.7 mg L^{-1}, and varied from 1.2 to 10.4 mg L^{-1} throughout the year. Two springs had median DOC values of 3.0 and 4.3 mg L^{-1}, and a surface stream had a median DOC value of 4.0 mg L^{-1}. SSH sites appear to be more variable but generally lower DOC values than surface habitats. A previous study of DOC in percolation water in PPCS resulted in a mean DOC value of 0.70+0.04 mg L^{-1}, and measurements from Organ Cave indicated a mean value of 1.10+0.15 mg L^{-1}. These results suggest that organic carbon in aquatic SSHs is lowest in epikarst.

VARIABILITY OF GROUNDWATER FLOW AND TRANSPORT PROCESSES IN KARST UNDER DIFFERENT HYDROLOGIC CONDITIONS

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Groundwater flow in karst aquifers is often characterized by strong variability of flow dynamics in response to different hydrologic conditions within a short time period. Consequently, water table fluctuations are often in the order of tens of meters, differences in flow velocities between low- and high-flow conditions can reach ten or even more times. In dependence to respective hydrologic conditions groundwater flow also results in variations of flow directions, and thus in contribution of different parts of the aquifer to a particular spring. The described hydrological variability has many implications for contaminant transport and groundwater vulnerability. Groundwater level rising reduces thickness of the unsaturated zone and decreases protectiveness of the overlying layers. Higher water flow velocities reduce underground retention. Due to more turbulent flow transport and remobilization of solute and insoluble matter is more effective. During high-flow conditions there is usually more surface flow and hence more concentrated infiltration underground. Particularly in karst systems that show very high hydrologic variability, this should be considered to understand or predict karst aquifers hydrological behavior and to prepare proper protection strategies.

WHERE'S THE FIRE? AN ANALYSIS OF CARBON PRECIPITATES IN BLACK AND OTHER CAVES OF THE UPPER GUADALUPE MOUNTAINS, NEW MEXICO

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The dark precipitates in Black Cave in the Guadalupe Mountains of New Mexico have, until now, remained a mystery. After preliminary examination of speleothem samples on the scanning electron microscope and the ion microprobe at the Institute of Meteoritics at UNM, Albuquerque, the black coloring has, so far, been shown to be caused by particulate carbon. Due to its distribution within the cave, we reject the anecdotal interpretation that it has been transported into the cave by air currents during a fire event. Rather, we hypothesize that it is hydrological in origin. Given the significant width of the black banding within the speleothems that presumably represents a significant duration of infiltration and what appear to be plant fossils seen in SEM images, we further suspect that this particulate carbon is ash from previous forest fire episodes that has made its way into the cave through fractures in the limestone. Such a natural particulate tracer of flowpaths is plausible, but the details hinge on the transport process itself and limitations on particle sizes potentially mobilized by precipitation events. A laboratory and field approach is necessary to demonstrate the feasibility of particulate infiltration of the sort that we suggest. Currently, research is being done to see if the black precipitates in a nearby cave, Hidden Cave, are similar to those found in Black Cave. Later, Cottonwood Cave will also be examined. Further, we are culturing microorganisms from samples to determine any presence of iron or manganese oxidizing bacteria in case metal oxidation is playing a role in the coloration. Additionally, we are comparing the carbon isotopic ratios of the dark, presumptively organic, bands to the isotopic ratios of the lighter and lower carbon bands in an attempt to confirm or discount an incendiary origin of the carbon.

USING HYDROGEOCHEMICAL AND ECOHYDROLOGIC RESPONSES TO UNDERSTAND EPIKARST PROCESSES IN SEMI-ARID SYSTEMS, EDWARDS PLATEAU, TEXAS, USA

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The epikarst is a permeable boundary between the surface and subsurface environments and can be conceptualized as the vadose critical zone of epigenic karst systems. This epikarstic boundary is often thought of as being permeable in one direction only (down), but connectivity between the flow paths of water through the epikarst and the root systems of woody plants means that water can move both up and down across the epikarst boundary. However, the dynamics of these flows are complex and highly dependent on variability in the spatial structure of the epikarst, vegetation characteristics, as well as temporal variability in precipitation and evaporative demand.

Here we summarize some insights gained from working at several sites on the Edwards Plateau of Central Texas, combining isotopic, hydrogeochemical, and ecophysiological methodologies. 1) Dense woodland vegetation at sites with thin to absent soils (0-30 cm) is in part supported by water uptake from the epikarst. 2) Despite the large total water storage capacity of epikarst, tree transpiration typically becomes water-limited in summer, suggesting that evapotranspiration occurs only out of a fraction of the epikarst, such as the top one or two meters, depending on local conditions. 3) Deeper flow paths, such as those feeding cave drips, quickly become disconnected from the evapotranspiration zone. 4) Without large or continuous precipitation, deep infiltration and recharge does not occur in these systems, and recharge thresholds are strongly correlated with antecedent potential evapotranspiration and rainfall, suggesting control by the moisture status of the epikarst evapotranspiration zone. The deeper epikarst and unsaturated zone in this region can be conceptualized as a variably saturated system with storage in fractures, matrix porosity, and in shallow perched aquifers, all of which are inaccessible to the root systems of most trees, although woody vegetation may control recharge thresholds.

CARBON FLUX IN THE DORVAN-CLEYZIEU KARST: LESSONS FROM THE PAST TO GUIDE FUTURE RESEARCH

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While availability of carbon has long been considered important for karst food webs, surprisingly little is known about the spatial and temporal patterns of carbon flux in karst and its ecological consequences. The Dorvan-Cleyzieu karst was probably the first karst ecosystem in which carbon transport was studied from an ecosystem and ecological standpoint. Data regarding dissolved (DOC) and particulate (POM) organic carbon flux and concentrations from the late 1970s and 1990s were synthesized to address large scale patterns in carbon flux and the role of biological processing of carbon. These patterns are then linked to more recent studies of organic carbon transport and biological processes in karst. Carbon flux and concentration displayed high temporal variation on both annual and event scales at Dorvan, but with little obvious seasonality. Variation in carbon flux was spatially variable throughout the aquifer. Floods represent particularly dynamic times for both carbon flux and als microbial activity in the aquifer. Patterns of DOC and nitrate in aquifers and more recent experimental microcosms suggest strong biological coupling of C and nitrogen cycles in karst aquifers. There appears to be strong potential for advancing our understanding by linking hydrological models to data regarding organic carbon distribution, form and biological lability, and microbial processes. Such models may be used to then address multiple, interacting biogeochemical cycles in karst.

GROUNDWATER ECOLOGY OF ALLUVIAL RIVER FLOOD PLAINS

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Shallow alluvial aquifers of river flood plains represent the transition zone between deep, old (phreatic) and shallow, young ground waters. Food webs in alluvial aquifers may be composed of a surprising number of invertebrates, including insects, that have riverine and terrestrial life history stages (amphibionts) and others that are typically found in cave streams or phreatic aquifers (stygobionts). The ecosystem structure and function of shallow aquifer of the Nyack Flood Plain on the Middle Flathead River in Montana has been studied for over three decades. The river loses 30% of its flow into the aquifer at the upstream end of the flood plain but aquifer discharge downstream returns flow to the active channels and feeds spring brooks, ponds and wetlands within the flood plain. The aquifer is characterized by extremely high hydraulic conductivity, related to the open framework nature of the gravel-cobble substrata that reflects the legacy of cut and fill alleviation by the river. The aquifer food web contains 46 invertebrate species with an extremely diverse microbial assemblage as their trophic base. Productivity is carbon limited but during late summer portions of the aquifer are hypoxic. Aquifer invertebrates are extremely tolerant of hypoxia and some apparently are methanotrophic, based upon notably depleted 13C values in carcasses, presence of methane in some of the wells seasonally and positive methanogensis assays. The aquifer also strongly influences plant succession and woody plant growth interacts with flooding to influence sediment scour and deposition. Thus the Nyack flood plain, and systems like it, may be described as a 3-dimensional shifting habitat mosaic that produces a hot spot of biodiversity within the regional landscape. Similar floodplain aquifers are described for rivers in Kamchatka, Alaska, Washington and elsewhere in Montana and likely exist to some extent in all alluvial rivers. However, river flood plains are the most endangered landscapes on earth owing to dams, gravel mining, revetments and flow regulation.

SEASONAL INFLUX OF ORGANIC CARBON INTO MARENGO CAVE, INDIANA, USA

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Water samples from forest soils and a shallow underlying cave were collected for the hydrological year 1996-1997. The soil waters displayed little seasonal variability in their concentrations of organic substances compared to the cave drip-waters that yielded highest levels in the spring and autumn seasons. The organic substances were separated in three fractions: particular organic matter, fulvic acids and humic acids. The important controls on the amount of organic substances reaching the cave are the seasonal fluctuation in the volume of percolation waters and the soil's ability to provide organic material to these waters. Fluorescence measurements of the organic compounds isolated from these waters revealed shorter peak excitation and emission wavelengths for the cave waters than for the soil waters, a result of both the differences in concentration and significant changes in the proportional organic assemblages in the waters. Precipitation appears to affect the fluorescence in both waters, with the dry autumn producing the highest yields. Molecular size fractionation revealed the preferential removal of the larger hydrophobic compounds from the water before they reach the cave, resulting in the smaller hydrophilic compounds becoming the dominant fluorophore.

TESTING CARBON LIMITATION OF A CAVE STREAM ECOSYSTEM USING A WHOLE-REACH DETRITUS AMENDMENT

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Energy limitation has long been considered the primary factor influencing in situ evolutionary and ecosystem processes in cave ecosystems. Few studies, however, have provided adequate data to test this hypothesis, either because they have focused on specific ecosystem processes (e.g., decomposition) or trophic levels (e.g., microbes), or because they involved factors (e.g., organic pollution) that confound data interpretation. In this study, the energy-limitation hypothesis in cave ecosystems was tested explicitly using a detrital manipulation experiment. From February 2010 to February 2011, a 100-m reach of a carbon-poor cave stream was amended with corn-litter and the response in consumer biomass was followed relative to that of an upstream reference reach. During one year of pre-manipulation (February 2009 to January 2010), mean standing crop organic matter was 19 to 34 g ash-free dry mass [AFDM] m^{-2}. The corn litter amendment significantly increased mean standing crop organic matter in the manipulation reach to 423 g AFDM m^{-2}. Total macroinvertebrate biomass increased by more than 5 times following the litter amendment. Stable isotope analyses indicated that corn-derived carbon represented 16-73% of macroinvertebrate biomass depending on taxon, indicating that increases in consumer biomass were driven by assimilation of corn-derived carbon. However, biomass of facultative surface species significantly increased following the amendment, while the biomass of obligate cave species remained unchanged. Facultative species are adapted to energy-rich surface streams (e.g. *r*-selected life histories), while obligate-cave species are adapted to survive in the energy-poor cave environment (e.g. K-selected life histories). These differences in evolutionary history likely contributed to the differential response to the corn litter amendment. While cave communities per se have the ability to exploit short-term increases in energy availability, species-specific responses are dictated by differing selective pressures and resulting life-history traits.

THE ROLE OF KARST CONDUIT MORPHOLOGY, HYDROLOGY, AND EVOLUTION IN THE TRANSPORT, STORAGE, AND DISCHARGE OF CARBON AND ASSOCIATED SEDIMENTS

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Karst aquifers and conduits form by dissolution of carbonate minerals and the slow release of inorganic carbon to the surface environment. As conduits evolve in size, morphology, and position within the aquifer, their function and capacity change relative to the storage and transport of inorganic and organic carbon as sediment. Conduits serve mostly as transport mechanisms for sediments. Quantified data are sparse, but for conduits to function effectively there must be at least equilibrium in the amount of sediment entering and exiting the aquifer. If sediment discharge exceeds input, little sediment will remain underground. When natural declines in base level cease removing sediments and deposit calcite speleothems, these materials are stored until the rock mass is denuded.

While sediment storage is mostly transient in hydrologically active conduits, relative differences occur. Aquifers with conduits developed at multiple levels or as floodwater mazes store proportionately greater volumes of sediment. Hypogenic systems should store greater volumes of sediment than epigenic aquifers because they mostly discharge a dissolved load as opposed to both dissolved and suspended clastic loads. However, some hypogenic aquifers are diffusely recharged and receive and store little sediment from the surface.

The global volume of sediment and carbon stored in karst aquifers is estimated to be on the order of 2×104 km^3 and 2×102 km^3, respectively. The amount of carbon stored in paleokarst is not estimated, but paleokarst petroleum reservoirs might serve as efficient carbon sinks for global carbon sequestration. Hydrocarbon-depleted paleokarst reservoirs should provide substantially more storage per injection well than sequestration in non-paleokarstic rocks.

CARBON FLUXES IN KARST AQUIFERS: SOURCES, SINKS, AND THE EFFECT OF STORM FLOWS

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The dissolution of carbonate rocks by the action of carbonic acid, either lowering the surface landscape or creating cave passages in the subsurface, consumes carbon dioxide. Thus, superficially, it would appear that karst processes remove CO_2 from the atmosphere and transport it from the karst drainage basin, first to the surface river system, and ultimately to the ocean. More careful evaluation of the carbon flux through karst aquifer system reveals various sources and sinks along the flow path so that only a fraction of the possible carbon load actually leaves the basin.

The ultimate source of CO_2 is the atmosphere. However, much of the CO_2 that drives karst processes is derived from decaying organic matter in the epikarst. The organic matter in turn was derived from vegetation that had sequestered CO_2 from the atmosphere at some earlier time. Measurements of soil CO_2 show values as much as 100 times the atmospheric value. The vegetative cover of the karst area is, therefore, an important amplifying factor in the CO_2 flux.

The main reaction site is the bedrock/regolith interface in the epikarst where the CO_2 from the overlying soil is consumed by reaction with the carbonate rocks. The carbon is carried as bicarbonate ions through the vadose zone to the water table. The vadose waters that intercept underlying cave passages can de-gas CO_2 into the cave atmosphere and precipitate speleothems. The cave air CO_2, typically about ten times the surface atmosphere, by diffusion and by circulating air currents, looses the CO_2 back to the surface atmosphere. There are data on the chemistry of seepage waters but flow rate data are sparse making it difficult to calculate this contribution to the overall carbon flux.

The load of inorganic carbon carried by seepage waters and cave streams is simply the sum of individual carbon species:

$$C_T = [CO_2(aq)] + [H_2CO_3] + HCO_3^-] + [CO_3^{-2}]$$

It is necessary only to assume equilibrium among the carbon-bearing species. The saturation state of the water does not enter the calculation. The total carbon flux can then be calculated from pH, dissolved bicarbonate, and discharge.

$$F_C = 17.012\, C_{HCO_3} \left\{ 1 + \frac{\gamma_{HCO_3}\, 10^{-pH}}{K_1} \right\} Q$$

In the chosen units, FC is the carbon flux in kg/day, the bicarbonate ion concentration is in mg/L, and the discharge, Q, is in m^3/sec.

The largest available collection of data is that for karst springs for which there are many chemical analyses, some with corresponding discharges. Carbon loads at the spring can be estimated and, assuming that half the carbon is released from dissolved limestone and dolomite, the other half is an estimate of the CO_2 that has been extracted from th atmosphere keeping in mind the cycling through the vegetative system. Storm flows typically dilute the dissolved carbonates but the increase in Q on the storm hydrograph more than offsets the decrease in C_{HCO3}.

Unfortunately, springs do not usually denote the downstream end of the karst system. Many springs discharge into spring runs which may flow for considerable distances before their confluence with rivers or the ocean. Water chemistry can change significantly along the spring run. Typically, CO_2 is de-gassed back to the atmosphere with a corresponding rise in pH. Some springs and spring runs de-gas sufficient CO_2 to oversaturate the water and cause the precipitation of tufa. Thus the carbon load that finally leaves the karst basin is substantially smaller than might be estimated from the overall bulk chemistry of carbonate dissolution.

HYDROGRAPH INTERPRETATION - CHANGES IN TIME

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Temporal variations in the discharge and in water quality parameters of water at springs have been one of the main, if not the main, method by which karst hydrologists have attempted to gain insight about the functioning of springsheds. Springs are ideal locations for such monitoring as the variations in the lateral outputs integrate physical, geochemical, and biological processes that have occurred throughout a particular springshed. The questions are, and have been, "How to interpret those records?" and "Can knowledge gained about processes occurring within one springshed be used to understand processes occurring in another basin?". This talk is an attempt to summarize how our use of hydrographs and our interpretations of hydrographs have changed since the 1960s.

KARST CONDUIT-MATRIX EXCHANGE AND THE KARST HYPORHEIC ZONE

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The exchange of water and solute between karst conduits and surrounding matrix is poorly quantified, as is its related biogeochemistry. Existing qualitative studies of exchange focus on spatial scales of hundreds of meters to kilometers, and on transient conduit floods. The physics of fluid flow suggest that conduit-matrix exchange should also exist at smaller scales caused by conduit tortuosity on the scale of 10s of meters, conduit wall morphology on the scale of meters, and wall morphology and conduit turbulence and transverse mixing on the scale of centimeters. When these smaller-scale processes occur for surface streams they are referred to as "hyporheic exchange." Borrowing the same name for karst aquifers, we refer to the matrix where these small-scale exchange processes occur as the "karst hyporheic zone." Using quantitative models, computational fluid mechanics, and a review of published qualitative studies we examine and characterize exchange processes ranging in scale from those caused by conduit floods to hyporheic exchange created by steady-state pressure variations induced by wall morphology, and compare and contrast them to analogous processes of exchange for surface streams. We focus on exchange for phreatic conduits in eogenetic karst, but comment on processing of nutrients, organic carbon, and contaminants, and reflect on implications for speleogenesis, vadose conduits and streams, and conduits and matrix in telegenetic karst.

THE STABILITY OF CARBON SINK EFFECT RELATED TO CARBONATE ROCK DISSOLUTION: A CASE STUDY OF THE CAOHAI LAKE GEOLOGICAL CARBON SINK

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In recent years, there have been more and more debates concerning karst carbon sink or source, and the key problem is whether the bicarbonate from carbonate rock dissolution is stable. With the Caohai Lake basin as the study area, on the basis of previous research, and by utilizing the carbon isotope model, the authors conducted studies and found that 58.8% of the bicarbonate is utilized by aquatic plants. The Caohai basin geological carbon sink amount is 588.67 tC/a. Submerged plants of lakes along the middle and lower reaches of the Yangtze River can fix 370,602 tC/a of carbon, and this means that every year 750,000 tons of CO_2 from geological weathering will be stabilized by submerged plants. So carbon sink effect related to carbonate rock dissolution is quite stable and the new karst dynamic system is rational.