

Report as of FY2006 for 2006AR137B: "A hydrogeological investigation of nitrate processing within a karst watershed"

Publications

- Conference Proceedings:
 - Brahana, John V., Tiong Ee Ting, Mohammed Al-Qinna, John F. Murdoch, Ralph K. Davis, Jozef Laincz, Jonathan J. Killingbeck, Eva Szilvagy, Margaret Doheny-Skubic, Indrajeet Chaubey, Phillip D. Hays, Greg Thoma, 2005, Quantification of Hydrologic Budget Parameters for the Vadose Zone and Epikarst in Mantled Karst, "in" U.S. Geological Survey Karst Interest Group Proceedings, Rapid City, South Dakota, p. 144-152.
 - Hays, Phillip, Jozef Laincz, Byron Winston, Susan Ziegler, Indrajeet Chaubey, Tim Kresse, Van Brahana, 2005, Elucidation of N-Processing within a Mantled Karst Watershed, "in" U.S. Geological Survey Karst Interest Group Proceedings, Rapid City, South Dakota
 - Ziegler, Susan, Byron Winston, Jozef Laincz, Phillip Hays, Tim Kresse, John Fazio, 2005, The extent and variability of biogeochemical processing within a mantled karst watershed, AWRC Conference Proceedings [CD].
 - Laincz, Jozef, 2005, A biogeochemical/hydrological approach to characterize transport and cycling of nitrogen in mantled karst watershed: AWRC Conference Proceedings [CD].
 - Hays, Phillip, Jozef Laincz, Byron Winston, Susan Ziegler, Indrajeet Chaubey, Tim Kresse, Van Brahana, 2006, Elucidation of N-Processing within a Mantled Karst Watershed, AWRC Conference Proceedings [CD].
 - Laincz, Jozef, Phillip Hays, Byron Winston, Susan Ziegler, 2004, A coupled biogeochemical/hydrological approach for elucidating transport and cycling of nitrogen within mantled karst watersheds, Arkansas Watershed Advisory Group Conference Proceedings, Little Rock, Arkansas.
- Other Publications:
 - Laincz, Jozef, Byron Winston, Susan Ziegler, Phillip Hays, 2004, A coupled biogeochemical/hydrological approach for elucidating transport and cycling of nitrogen within mantled karst watersheds, Geological Society of America Abstracts with Programs, Vol. 36, No. 5, p. 258.
 - Laincz, Jozef, Byron Winston, Susan Ziegler, Phillip Hays, Tim Kresse, John Fazio, 2005, A Biogeochemical/hydrological approach to characterize transport and cycling of nitrogen in mantled karst watersheds, Geological Society of America Abstracts with Programs, Vol. 37, No. 7, p. 28.
 - Hays, Phillip, Susan Ziegler, Jozef Laincz, Byron Winston, 2006, Nitrogen Transport and cycling in the interflow zone of a mantled karst watershed in Northwest Arkansas, Geological Society of America Abstracts with Programs, Vol. 38, No. 7, p. 195.
 - Winston, Byron, Jozef Laincz, Susan Ziegler, Phillip Hays, 2005, Biogeochemical Processing of N in a Mantled Karst Watershed, Eos Trans. AGU, 86(18), Jt. Assem. Suppl., Abstract H43D-04.
- Dissertations:
 - Winston, Byron, 2006, "MS Thesis," Department of Biological Sciences, Fulbright College of Arts and Sciences, University of Arkansas, Fayetteville, Arkansas, 88p.

Report Follows

13. Source and transformation of nitrate within a karst watershed.

14. STATEMENT OF PROBLEM

An understanding of the hydrogeological and biogeochemical processes controlling transport and processing of nutrients in karst watersheds is critical to the design of effective nutrient management and agriculture practices. Rapid growth of poultry and swine production has occurred in karst regions of the U.S. where soils are thin and underdeveloped (NASS 1999). Manure from animal feeding operations in these areas is typically utilized through application to pasture (McLeod and Hegg 1984). These trends have resulted in the transport of excess levels of the nitrogen (N) to surface and ground waters, particularly in karst terrain (Vervoort et al. 1998; Boyer and Pasquarell 1999). Nitrogen is implicated in serious problems of human health and regional to national scale ecosystem viability which have critical bearing on sustainability of current agricultural practices (Spaulding and Parrott 1994; Malakoff 1998; Rabalais 2002). Unfortunately, knowledge regarding the source and biogeochemical processes controlling N transport in karst systems lags far behind that of other surface- and ground-water systems. Our understanding of soil nutrient dynamics may be effectively applied to karst terrain, however, soil processes often represents a small fraction of the N processing due to the poorly developed soils typical of karst. Lateral, diffuse flow occurring at permeability contrasts, defined as the interflow zone, represents a potentially important but poorly understood flow path with respect to transport and biogeochemical processing. The fact that land-use activities and potential conservation practices have the largest impact upon soil and interflow zones in karst watersheds stresses a need for knowledge of the hydrological and biogeochemical processes occurring within the interflow zone. Key information needed for understanding such systems and which will be accrued for the proposed study includes delineation of flow paths through application of tracer and flow monitoring techniques and assessment of nitrate transformation using isotopic analyses.

15. STATEMENT OF RESULTS OR BENEFITS

Results of this watershed-scale study and findings of future studies enabled by these initial steps in characterizing biogeochemistry of agriculturally impacted karst will be exportable to many karst settings where agricultural land use is important (NASS 1999). The soil and interflow zones of karst watersheds are vulnerable to agricultural practices. The proposed research will demonstrate the role of specific surface to subsurface zones in biogeochemical cycling of N and the connectivity of these zones to downstream ecosystems. These results will provide a means to understand the impact that hydrologic alteration of these zones can have on delivery of nitrate to the subsurface, and provide a means to devise effective nutrient management and agricultural practices in these vulnerable landscapes. Once we gain a better understanding of nutrient biogeochemistry of the interflow zone, we will be poised to test how agricultural practices in karst watersheds impact the integrity of this zone and determine how processes occurring within the interflow zone may be capitalized upon for nutrient management in karst watersheds. A specific example of interest is the practice of rotational grazing which improves grazing as well as diffuse/focused flow recharge ratios. These results will be of great

use to USDA NRCS, State Cooperative Extension Offices, and other agencies concerned with the critical and expanding issue of nutrient management in karst landscapes.

16. NATURE, SCOPE, AND OBJECTIVES OF PROPOSED RESEARCH

The proposed research aims to investigate the importance of subsurface processes on nutrient dynamics in a well-characterized experimental watershed, the Savoy Experimental Watershed (SEW). The SEW, a 1250 ha property of the University of Arkansas (UA), was initiated in 1997 as a collaborative effort of UA, USDA-ARS and NRCS, and USGS. Previous studies at SEW suggest that runoff from upland pastures infiltrates into the subsurface and no surface runoff occurs from the basin during base flow. This is typical of karst terrain and emphasizes the importance of the subsurface flow component (Sauer et al. 1998; Brahana et al. 2000). Although soil pore-water concentrations of DOC and NO_3^- are often high due to manure application, analyses at SEW demonstrate very low DOC ($\sim 0.4 \text{ mg l}^{-1}$) and NO_3^- ($\sim 1 \text{ mg l}^{-1}$) base-flow concentrations at the seeps, which represent the end result of processing within the interflow zone.

This proposal outlines work which will be used to obtain more direct measures of the contribution of the interflow zone to the water budget by conducting tracer tests and monitoring of epikarst flow, and NO_3^- processing within an experimental karst watershed where preliminary data and samples currently exist. Our results from a study of sampling points representing water from the interface, interflow, surface and focus flow zones from a single plot within this watershed suggest removal of NO_3^- occurs within the interflow zone and ranges between 4 and 30% (depending upon flow path) when corrected for dilution. The extent of this removal, as determined by simple mixing models may be related to the relative bioavailability of dissolved organic carbon (DOC) as determined by measurement of groundwater community respiration relative to DOC concentration (Fig. 1). In addition to these indirect results samples have been collected for the N and O isotopic composition of nitrate. Only a small subset of these samples have been analyzed for the

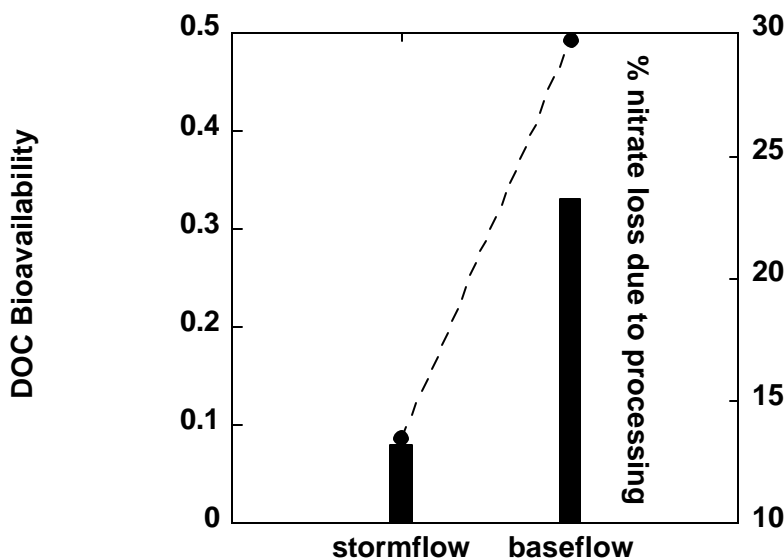


Figure 1. The mean relative bioavailability of dissolved organic carbon (DOC) in units of $\mu\text{M C h}^{-1}$ respired per mM C available as DOC (bars) and the proportion of nitrate loss within the interflow zone due to processing expressed as a percent of total loss due to dilution and processing (points) determined from analyses of water samples collected from 4 seeps in December 2004.

isotopic composition of nitrate as part of training the PI (Ziegler) in a new method (Sigman et al 2001). This approach uses a genetically modified denitrifier (*P. auerofaciens*) to convert NO_3^- in a water sample to N_2O which is subsequently analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ on a gas preparation devise interfaced to a isotope ratio mass spectrometer (IRMS). Samples were prepared and analyzed by Ziegler at the USGS Stable Isotope Laboratory in Reston, Virginia under the advisement of Ty Coplen and his staff. This training was instrumental in our current set up now running in the UA Stable Isotope Laboratory where we are just now beginning to be able to analyze samples for the analysis of nitrate in water. The data analyzed in the Reston lab suggests that nitrate processing may be occurring in the interflow zone (Fig. 2). The additional analyses of nitrate isotopes in conjunction with tracer studies to identify the links between the plot and our interflow sampling points will enable us to establish the role of the interflow zone in the (1) overall water budget of the plot studied, and (2) processing of nitrate. Our preliminary data provide for indirect conclusions, direct investigation of the processes occurring within the hydrologic zones of this watershed are necessary to establish the importance of interflow in determining the fate of nutrients within karst watersheds.

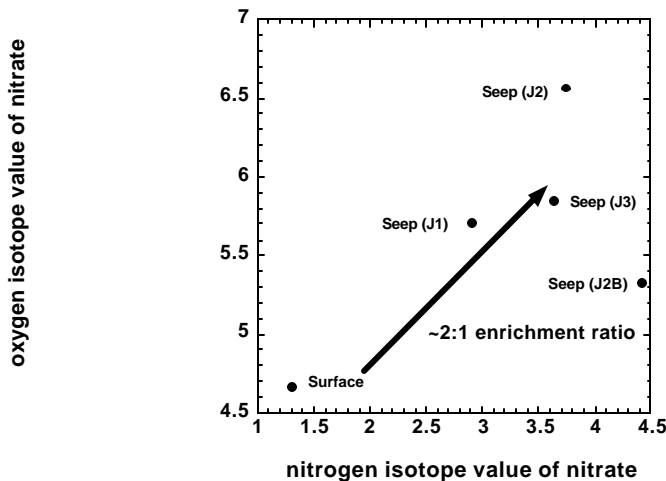


Figure 2. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate (‰) collected following a storm event in July 2004 from a surface runoff trough and the four major seeps draining the study plot at the Savoy Experimental Watershed. The line approximates the shift from the surface to the seeps which integrate the interflow zone and suggests a n enrichment indicative of denitrification which often results in a 2:1 ratio for N versus O.

Objectives

The objective of this study is to elucidate the importance of the interflow zone as a site for the biogeochemical processes controlling NO_3^- transport in karst watersheds. The plot scale quantification of nutrient transport proposed will enable us to identify the role of specific hydrological zones in processing NO_3^- . This basic information will enable us to develop a larger scale study to include multiple field plots subjected to agricultural practices commonly utilized in the agricultural regions of the United States underlain by karst hydrology. The hypotheses to be tested by the proposed research are:

1. The interflow zone is both an important part of the water balance and a significant pathway for the transport of nutrients in the SEW.
2. The interflow zone is a region of nitrate uptake characterized by enrichment in the N and O isotopes of nitrate.

Experimental Plan

The proposed research will be conducted in the SEW and enable us to address specific, well-constrained flow paths. Hydrogeologic research at the SEW has resulted in a sampling infrastructure and large data set that will provide an excellent foundation for the proposed research (see website <http://www.uark.edu/depts/savoyres> for maps of the site and data). The proposed approach will focus on one plot (100 m²) and the interflow and focused flow pathways below it, enabling accrual of detailed process information at the plot scale. As part of the proposed research samples collected using this sampling structure will be used, taking advantage of the geochemical and biological data previously collected and interpreted (see below and Related Research). Additionally, we will conduct tracer studies to more specifically characterize the relationship between the plot and groundwater zones. This study will enable us to design a future larger scale study using multiple plots and different land use treatments in order to scale our findings up to the watershed scale and investigate the impact of land use on nitrate processing and transport.

Hypothesis 1: The interflow path represents an important part of the water balance and pathway for the transport of nutrients within the study plot.

Direct measurement of water at the base of the soil and regolith zones and flowing through the interflow zone will be conducted to assess the role of interflow in both the water budget and transport of nutrients. Flow monitoring and tracer tests will be employed to quantify the local flow budget and show the lateral component of interflow imposed upon water moving into the subsurface. Concurrent water samples from the interflow zone, and focused-flow ground water down gradient from the plot will be collected during both base-flow and storm

events. Additionally, a surface-runoff sample will be collected during two storm events from surface drains installed at the lower end of each plot, and rainfall will be measured at the Savoy weather station. Water from each sampling point will be measured for T, pH, conductivity, and dissolved oxygen. Water samples will be analyzed for NO_3^- , PO_4^{2-} , total and dissolved organic carbon, dissolved inorganic carbon, Br^- , Cl^- and the δD and $\delta^{18}\text{O}$ of water.

Flow data will be collected and analyzed to determine the proportion of incoming precipitation transported in the interflow path. Interflow will be sampled and quantified at the plot scale above permeability contrasts created by the epikarst surface, relict chert layers, and soil fragipan. A trench has been constructed and successfully used as part of past sampling experiments involving this plot. Interflow samples will be collected from both interceptor drains installed at the permeability contrast on the lower plot boundary, and at seeps located down gradient from the runoff plot. The seeps, positioned above the focused-flow dominated flow path, have been shown to integrate flow from interflow zones and therefore define the terminus of flow that is “short circuited” onto the interflow path (Brahana et al, 2000). Focused-flow ground water will be sampled at the spring using a dedicated autosampler. The sampler will be manually activated to sample during the base-flow sampling and will automatically collect flow-weighted samples across the hydrograph curve during storm events. Samples described above will be collected two times during base flow conditions to determine seasonal variability in connectivity between the study plot and interflow zone. Samples will also be collected during two storm events representing varying antecedent hydrologic and saturation conditions. These samples will be used to determine the degree to which flow within the interflow zone is reduced during storm events. Storm flow is characterized by high flow resulting in increased focused flow and shorter residence time.

To address the complexity of quantifying the hydrologic budget during storm events and facilitate further understanding of the subsurface interflow processes, tracer experiments utilizing the δD and $\delta^{18}\text{O}$ of water and inorganic tracers (Br^- and Cl^-) will be conducted after two storm events. Storm precipitation often yields a unique stable isotopic composition as compared with ground water, thus providing a usable, adventitious tracer. Anion tracers Br^- and Cl^- will be used to calibrate the stable isotopic tracer method and corroborate results. Mixing curves incorporating precipitation, interflow, and focused-flow ground water and post-storm isotopic compositions will enable accurate characterization of water movement. Rain samples will be collected during the two storm events. After each storm event, water samples will be collected on an hourly basis for 24 hours after the established breakthrough times determined from a Br^- and Cl^- tracer study at the plot. The Br^- - and Cl^- -tracer study will be similar in design to those of Buchter et al. (1997) and will be completed once prior to each major storm event sampled. Samples will be collected from the seeps, a trench intersecting the permeability contrast, and two springs and Cl^-/Br^- breakthrough curves will be generated.

Hypothesis 2: The interflow zone is a region of nitrate uptake signified by enrichment in the ^{15}N and ^{18}O of nitrate. Denitrification is the main route by which bioreactive N is removed from natural systems. The prevalence of this process in ground-water will depend upon DOC bioavailability, NO_3^- and oxygen concentration. We expect this process to be important when transport of DOC is highest and microzones of anoxia are established as a

result of aerobic respiration of DOC within the subsurface matrix. Concentration and stable isotopic composition of NO_3^- in samples collected as part of the sampling regime outlined above will be used to assess the relative importance of nutrient uptake in each hydrological zone. Analyzing NO_3^- isotopic composition in two dimensions ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) will provide evidence for denitrification occurring within each flow path (Mayer 2002; Silva et al. 2000). The importance of denitrification to the removal of NO_3^- within the interflow zone will be determined by combining our mixing model results using conservative tracers (Cl- and Br-) with the isotopic composition of NO_3^- . We currently have a suite of samples covering the interface, interflow and focus flow zones for 2 storm events and 5 base flow sampling events collected from June 2004 through June 2005. Geochemical data and use of a simple mixing model suggests that processing occurring within the interflow zone removed up to 10% of nitrate passing through that zone and that reduction in NO_3^- within the interflow zone can represent as much as 30% of total losses of NO_3^- . We hypothesize that the isotopes of nitrate will be enriched in ^{15}N and ^{18}O in water from the seeps relative to the surface inputs. In fact the small subset of data we do have at this point, from a storm event in July 2004, suggests this may be the case (Fig. 2). We cannot rule out the possibility that immobilization of N by microorganisms within the interflow zone may be an important process removing NO_3^- in transport. This process, however, represents only a temporary sink for N. If immobilization is in fact the dominant mechanism for removal of NO_3^- from the system we will see NO_3^- losses along the flowpath without the 2:1 ratio of change in N versus O isotopic composition of nitrate. This would provide us with vital information regarding the cycling of N within these groundwater systems enabling us to provide better information upon which to base land use management practices to reduce nutrient transport to down stream ecosystems (e.g. Illinois River).

16. METHODS, PROCEDURES, AND FACILITIES

Sample Handling and Analyses.

Sampling equipment, materials, decontamination procedures, and sampling procedures will follow stringent USGS-developed low-level sampling protocols (Wilde et al., 1998) developed for obtaining representative and consistent data at the National level. Prior to collecting samples the pH, T, conductivity and dissolved oxygen concentration will be determined for each sampling point using a YSI63 and YSI550A (Yellow Springs, OH)

Total and dissolved organic carbon will be determined using high-temperature combustion with a Shimadzu TOC5050. The Shimadzu 5050 will also be used to determine dissolved inorganic carbon concentrations. Nitrate, phosphate, and ammonium concentrations will all be determined using a flow injection analysis system with colorimetric detection using a Lachat 8500.

Stable isotopic composition of NO_3^- will be determined for samples (20 mL) following the method of Sigman et al 2001. Cultures of *Pseudomonas aureofaciens* (ATCC# 13985)

obtain from ATCC are currently maintained and stored (-80°C) in the Ziegler lab. Briefly, starter cultures will be established from the second and third plating of the original culture and used to generate larger cultures which are grown up in sterilized, sealed media bottles until they become anaerobic and exhaust the supply of nitrate provided. These large cultures will be centrifuged to generate a concentrate of the denitrifier which will be dispensed in 3 mL aliquots into a series of 20 mL vials, sealed with an aluminum backed septa, and purged with He for 30 minutes. Once purged vials will be injected with 1 mL of water sample or standard containing 20 nmol of NO_3^- and incubated for 24 h. Following this incubation the vials are analyzed for the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the N_2O on a modified Gas Bench II interfaced with a Delta XP isotope ratio mass spectrometer.

Stable isotopic analyses of water for δD and $\delta^{18}\text{O}$ will be conducted on a isotope ratio mass spectrometer (Finnigan Delta^{XP}; UA Stable Isotope Facility) interfaced with a high temperature pyrolysis analyzer (Finnigan TCEA).

Facilities.

Dr. Ziegler maintains a lab in the Department of Biological Sciences containing all equipment necessary to prepare water samples for chemical and isotopic analyses required for the work described. She maintains a Lachat 8500 flow injection system for the analysis of NO_3^- , NH_4^+ , SRP and total phosphorus, a Shimadzu TOC5050 for total organic and inorganic carbon determination in water samples, centrifuges, vortexers, balances, pipettors, and incubators needed for NO_3^- isotope sample preparation as well as probes for field measures. Dr. Hays maintains the Geosciences Geochemistry lab with all equipment necessary for tracer experiments, and water quality sampling The UA Stable Isotope Laboratory (UASIL), located next to Ziegler's lab, houses three continuous-flow isotope ratio mass spectrometers (Finnigan Delta⁺): One mass spectrometer is interfaced with a pyrolysis EA unit and autosampler for analysis of $\delta^{18}\text{O}$ and δD of water samples. The same mass spectrometer is also interface to a gas preparative devise allowing for the separation of N_2O from CO_2 . This devise (ThermoFinnigan Gas Bench II) has been modified by Ziegler to simultaneously purge, sample, and strip samples of CO_2 , water and organics for the analysis of N_2O for N and O isotopic composition. The system has been tested and is recently being used to analyze groundwater samples for the isotopic composition of nitrate following the preparation outlined above. All equipment for preparation of stable isotope analysis is present within the UASIL facility or Ziegler's lab. Additionally, the SEW is a modern research facility with field laboratory and equipment for extensive hydrogeologic investigations: 2 Giddings hollow-stem auger drilling rigs (cooperative agreement with USGS); mobile field geochemistry lab; 3 compound v-notch/rectangular weirs; H-flume ; 4 Campbell Scientific dataloggers; weather station; 8 water-level pressure transducers; 6 Sigma 900 autosamplers; 1 backhoe, 2 4x4 field vehicles.

17. RELATED RESEARCH

Understanding the interplay of the hydrogeology and biogeochemical processes that control transport and processing of nutrients in karst watersheds is critical to the design of

effective nutrient management and agriculture practices. Our understanding of these processes in karst systems, however, lags considerably behind that for other aquatic ecosystems (e.g. marine ecosystems Ziegler and Benner 1999; surface water Bernhardt and Likens 2002; granular aquifers Chapelle 1992). Karst hydrogeology is typified by a carbonate rock framework containing a network of dissolution features resulting in very high permeability and a predominance of focused flow of ground water (Fig. 3). Focused flow moves organic matter and nutrients rapidly through the system and affords limited opportunity for retention and biogeochemical transformation. Natural attenuation is therefore dependent upon zones, such as the unsaturated zone in soil and regolith and interflow zones occurring at permeability contrasts, where diffuse and lateral flow does occur (Fig. 3). However, nutrient transport and processing mechanisms in these potentially important zones, and particularly the interflow zones, remain poorly

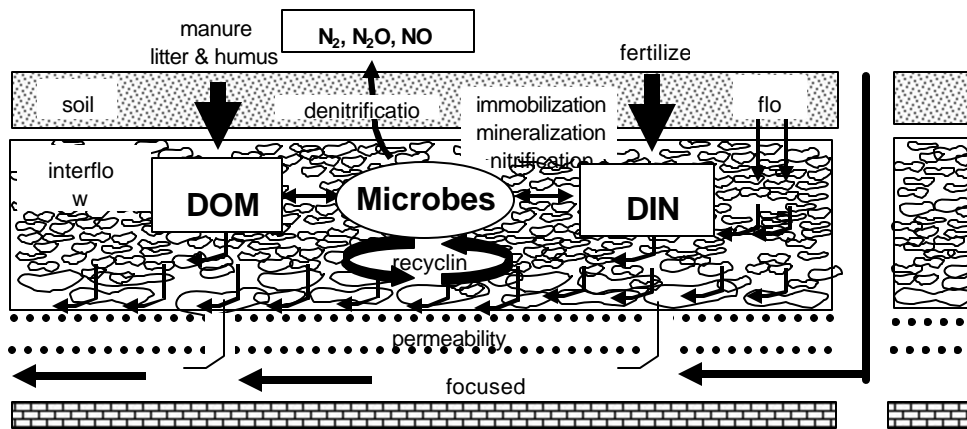


Figure 3. Conceptual diagram of hydrogeological flowpaths and the proposed biogeochemical cycling occurring within surface-subsurface zones within karst terrain. Reservoirs of dissolved organic matter (DOM), dissolved inorganic nitrogen (DIN), and gaseous forms of nitrogen are all illustrated.

understood. The soil, regolith, and interflow zones are characterized by longer water retention time and greater matrix/water ratios that may increase the extent of biogeochemical processing. These zones can often be regions of increased microbial activity and nutrient transformation due to physicochemical contrasts created by the mixing of water types (Madsen 1995; Gayte et al. 1999). In addition to being regions of elevated microbial activity and biogeochemical processing, soil, regolith and interflow zones are likely to be the most impacted by agricultural practices occurring on the surface. The soil/regolith unsaturated zone in karst constitutes the hydrogeologic zone where vertically migrating waters infiltrate to the subsurface. In most karst watersheds, however, the soil is poorly developed and may not provide substantial nutrient processing (Vervoort et al. 1998). This feature emphasizes the importance of interflow in karst settings. In zones of interflow, increased water residence times result from horizontal flow caused by the presence of permeability contrasts (e.g. fragipans, relict insoluble layers of chert, the epikarst surface). The increased water residence time makes the interflow zone a potentially

important region of increased microbial activity and nutrient cycling especially in karst watersheds with poorly developed soil.

Availability of dissolved organic matter (DOM), a likely control in biogeochemical cycling of nutrients within the interflow zone, is easily altered by agricultural practices in karst watersheds (Madsen and Ghiorse 1993). Dissolved organic matter composition can impact the rates and relative importance of key processes in the N cycle. When dissolved inorganic nitrogen (DIN) is abundant, for example, bacterial growth is usually stimulated by the addition of DOM, and often results in a decrease in DIN (Amon and Benner 1996; Ernstsens et al. 1998; Bernhardt and Likens 2002). Limits on N cycling set by carbon are an important feature of ground water. Nitrate concentrations, for example, have been found to be less important than organic C content for determining levels of denitrification in groundwater systems (Puckett and Cowdery 2002; Starr and Gillham 1993; Drury et al. 1991). DOC, a quantitative measure of DOM, is therefore likely to be an important and measurable factor controlling the N-cycling in karst terrain. In agricultural soils, subsurface DOC often represents the largest pool of actively cycling C fueling subsurface microbial activity (Campbell et al. 1999; Chardon et al. 1997; Boyer and Groffman 1996). In our previous work at the proposed study site we observed periods when concentrations of DOC from the interflow were elevated relative to the focused flow paths during baseflow (Fig. 4). Hydraulic properties of soil and the subsurface environment influence DOM

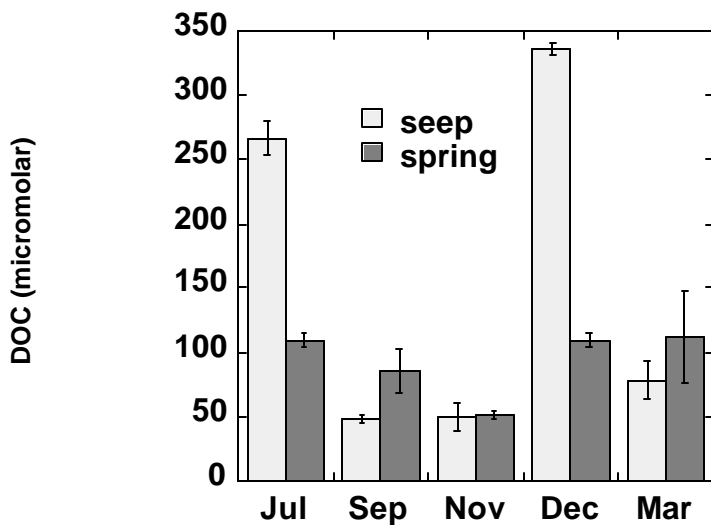


Figure 4. Mean dissolved organic carbon (DOC) concentration from 4 seeps and 2 springs down gradient from the proposed study plot within the Savoy Experimental Watershed 2004-2005 during base flow. Error bars represent one standard deviation.

source and bioavailability via transport mechanisms and stimulation of biotic and abiotic processing. Thus, land-use activity is likely to have far reaching implications for biogeochemical cycling of N in karst watersheds by influencing hydraulic properties. Advocates of rotational grazing, for example, postulate that the practice improves foraging due in part to reduced compaction of soils. Additional benefits of this practice may also include the preservation of greater hydraulic conductivity and better connection between the surface, soils and interflow zones, resulting in: 1) less precipitation being shunted to surface runoff and focused flow pathways, 2) more water moving through soil and regolith and interflow zones and 3) greater levels of manure-derived nutrient processing.

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19. TRAINING POTENTIAL

The proposed research will assist in the program of two graduate students. One student, Byron Winston, directed under the advice of Susan Ziegler (Biological Sciences), has been investigating the biogeochemical aspects of this work as part of his M.S. thesis. Mr. Winston has been working directly with the NO_3^- isotope method, growing the cultures, preparing the N_2O samples, and learning to run the isotope ratio mass spectrometer in the UASIL. Funding from this proposal will enable Mr. Winston to analyze the remaining samples and test hypothesis #2 proposed. Jozef Laincz is current working toward his Ph.D. in the Environmental Dynamics Program under the advice of Phil Hays (Geosciences) emphasizing the hydrological aspects of the proposed work as part of his Ph.D. dissertation. We anticipate this project will also involve a couple of undergraduate students in each department given the nature of the research and the current student involvement in ongoing projects. The SEW has served as the focus site of the annual UA/USGS Field Hydrogeology course offering intensive field training for students and young USGS hydrologists (see website <http://www.uark.edu/depts/geology/geology.htm>); installation, monitoring, and sampling activities at the proposed plot/flow path study site will provide for additional educational exposure in the field hydrogeology course.

20. STATEMENT OF GOVERNMENT INVOLVEMENT

Dr. Phillip D. Hays, a U.S. Geological Survey Hydrologist with the Office of Ground Water, will be a collaborator on this project. Currently, he is assigned (half-time) to the UA as a Visiting Scientist, conducting hydrologic projects and research mutually benefiting USGS and UA missions. Dr. Hays has worked with the PI to develop the conceptual model behind this study, the study work plan and proposal, as well as being involved in previous USGS efforts at SEW and the UA/USGS Field Hydrogeology course. Hays and Ziegler have recently completed a USDA funded SEED project at the Savoy site which resulted in the data and samples that will be used in this current proposed work. For this study, Dr. Hays will oversee all elements described in this proposal involving hydrologic characterization. This will involve installation of water-quality sampling equipment on the plot, design and execution of the tracer studies, water-quality sample collection and analysis, and interpretation and reporting of results. Dr. Hays is currently advising a geosciences graduate student involved in this research. Dr. Hays will receive no funding from this proposed work nor will his time or other resources be applied as matching funds.

In addition to the direct involvement of a USGS scientist, the newly established denitrifier method for the isotopic analysis of NO_3^- in the UA Stable Isotope Laboratory is the result of interaction with scientists at the USGS Reston Stable Isotope Laboratory (<http://isotopes.usgs.gov/>). We anticipate a continuation of this relationship which has benefited our research program and particularly the research outlined in this proposal. A great deal of resources have gone into setting up this new method and we are now in a position to reap the benefits of this development by utilizing this method in the work outlined in this proposal.

21. INFORMATION TRANSFER PLAN

Results will be of great interest across a broad, multidisciplinary audience including environmental hydrologists, biologists, and sustainable agriculture scientists and planners. Results will be presented in a commensurately broad group of journals, reports, and meetings. Interim results are to be presented at GSA, AGU, USGS Karst Interest Group meeting and the Karst Waters Institute annual meetings. Final results will be published in *Ground Water* and *Biogeochemistry*. Results with agricultural applications will be reported in an NRCS National Water Management Center Technical Series publication and Summary Fact Sheet as well as being placed on the NRCS-NWMC website. Agricultural aspects will also be presented at the NRCS-sponsored National Watershed Coalition Annual Meeting, to target NRCS and State Cooperative Extension Agency personnel.

22. INVESTIGATOR'S QUALIFICATIONS

Susan E. Ziegler

Department of Biological Sciences
622 Science Engineering
University of Arkansas
Fayetteville, Arkansas 72701
U.S.A.

Phone: (O) 479.575.6944
(L) 479.575.6342
Fax: 479.575.4010
Email: susanz@uark.edu
Web: www.uark.edu/~susanz/

Education

B.S. 1993 University of Massachusetts at Amherst – Environmental Science
Ph.D. 1998 University of Texas at Austin - Marine Science
Postdoctoral 1999 Carnegie Institution of Washington - Geophysical Laboratory -Fellowship
Stable Isotope Biogeochemistry

Professional Experience

2005-present **Associate Professor**, Dept. of Biological Sciences, Univ. of Arkansas
2002-present **Co-director**, University of Arkansas Stable Isotope Laboratory
2000-present **Assistant Professor**, Dept. of Biological Sciences, Univ. of Arkansas
1998-1999 **Postdoctoral Fellow**, Carnegie Institution of Washington

Relevant Publications

- Ziegler, S.**, White, P. M., and D. C. Wolf (2005) Tracking the fate and recycling of a ^{13}C -labeled substrate in soil: Lessons for stable isotope-labeling and biomarker studies. (in press) Soil Science
- Billings, S. and **S. Ziegler** (2005) Linking microbial activity and soil organic matter transformations in forest soils under elevated CO_2 . In press Global Change Biology 11:
- Brisco, S. and **S. Ziegler** (2004) Effects of solar radiation on the utilization of dissolved organic matter in Ozark headwater streams. Aquatic Microbial Ecology 37: 197-208.
- Ziegler S.**, Kaiser E. and R. Benner (2004) Seasonal and diel dynamics of dissolved organic nitrogen and phosphorus in a subtropic seagrass-dominated lagoon. Bulletin of Marine Science 75(3): 391-407
- Ziegler S.** and S. Brisco (2004) Relationships between the isotopic composition of dissolved organic carbon and its bioavailability in contrasting Ozark streams. Hydrobiologia 513: 153-169.
- Schaeffer, S.M., **S. Ziegler**, J. Belnap, and R.D. Evans (2002) Bromus tectorum invasion alters soil microbial carbon and nitrogen cycling in an arid Colorado Plateau grassland. , Eos. Transactions (suppl.) American Geophysical Union #B27A-0753.
- Ziegler S.** and M. L. Fogel (2003) Seasonal and diel relationships between the isotopic compositions of dissolved and particulate organic matter in a freshwater ecosystem. Biogeochemistry 64:25-52.

- Fogel, M. L., Teece, M. A., McCarthy, M., **Ziegler S. E.**, and Keil, R. G. (2000) Compound specific isotope signals in DOM and other geochemical reservoirs. *Eos Transactions (Supp.)*, American Geophysical Union, 80, OS12J-03.
- Ziegler S.** and R. Benner (2000) Effects of solar radiation on microbial production and dissolved organic matter cycling in a shallow, subtropical lagoon. *Limnology and Oceanography* 45: 257-266.
- Benner R. and **S. Ziegler** (2000) Do photochemical transformations of dissolved organic matter produce biorefractory as well as bioreactive substrates? *In Current Perspectives in Microbial Ecology*, C. R. Bell, M. H. Brylinsky, and P. Johnson-Green (eds). Springer-Verlag.
- Ziegler S.** and R. Benner (1999) Dissolved organic carbon cycling in a subtropical seagrass-dominated lagoon. *Marine Ecology Progress Series* 180:149-160.
- Ziegler S.** and R. Benner (1999) Nutrient cycling in the water column of a subtropical seagrass meadow *Marine Ecology Progress Series* 188: 51-62.
- Ziegler S.** and R. Benner (1998) Ecosystem metabolism in a subtropical seagrass dominated lagoon. *Marine Ecology Progress Series* 173: 1-12.
- Strom S., Benner R., **Ziegler S.** and M. Dagg (1997) Planktonic grazers are a potentially important source of marine dissolved organic carbon. *Limnology and Oceanography* 42: 1364-1374.

Relevant Presentations

- Winston, B., Laincz, J., Hays, P. and **S. Ziegler**, 2005. Biogeochemical processing of N in a mantled karst watershed. American Geophysical Union Joint Assembly. May 23-27, New Orleans, LA.
- Townsend, S. L. and **S. Ziegler**, 2005. The impact of solar radiation on the use of dissolved organic matter in two Ozark Streams: Possible role of photo-enhanced humification. American Geophysical Union Joint Assembly. May 23-27, New Orleans, LA.
- Ziegler, S.** and S. Brisco-Townsend, 2005. Stable isotope tracking of autochthonous carbon in two contrasting Ozark streams. American Geophysical Union Joint Assembly. May 23-27, New Orleans, LA.
- Piercey, G. L., Brisco, S. L. and **S. Ziegler**, 2005. Stable isotopic relationships among biofilm, algae, and dissolved organic matter in two Ozark streams: Spatial and temporal considerations. American Geophysical Union Joint Assembly. May 23-27, New Orleans, LA.
- Ziegler, S.**, Winston, B., Laincz, J., Hays, P., and T. Kressie. 2005. Use of stable isotopes for investigations of nitrogen processing within a karst watershed. Arkansas Water Resources Meeting. April 19, Fayetteville, AR.
- Laincz, J., Winston, B., Hays, P. and **S. Ziegler**, 2004. A coupled biogeochemical/hydrological approach for elucidating the transport and cycling of nitrogen within mantled karst watersheds. Geological Society of America Annual Meeting. 7-10 November, Denver, Co.
- Ziegler, S.E.** and S.L. Brisco (2004) Tracking autochthonous carbon in two contrasting Ozark streams using stable isotopes. North American Benthological Society Meeting. Vancouver, BC, Canada. June 6-10, 2004.
- Brisco, S.L. and **S.E. Ziegler** (2004) Effects of solar radiation on dissolved organic matter utilization in Ozark streams. North American Benthological Society Meeting. Vancouver, BC, Canada. June 6-10, 2004.

PHILLIP D. HAYS

Current Position: Hydrologist, U.S. Geological Survey, Water Resources Division

Correspondence: University of Arkansas, Geosciences Dept. Ozark Hall 113, Fayetteville, AR 72701 USA

Business Telephone: (501) 575-7343, Fax: (501) 575-3469

Email: pdhays@usgs.gov

Education:

Ph.D., Geology, Texas A&M University, 1992.

M.S., Geology, Texas A&M University, 1986.

B.S., Geology, University of Arkansas, 1984.

Professional Experience:

January 2000 – present, Hydrologist, U.S. Geological Survey, Visiting Scientist/Liaison to USDA Natural Resources Conservation Service National Water Management Center, Little Rock, Arkansas

- Ground Water Specialist providing assistance in ground-water hydrology and geochemistry to USDA NRCS customers nationally and internationally.
- USGS Liaison to NRCS providing enhanced communication between USGS and NRCS on issues of common interest, facilitating cooperation with USGS and use of USGS resources and data.

July 2000 – present, Associate Research Professor, USDA Natural Resources Conservation Service/U.S. Geological Survey Visiting Scientist with the University of Arkansas Department of Geosciences, Fayetteville, Arkansas

- Research: hydrogeology and stable isotope hydrogeology, agricultural water supply and water quality systematics, nutrient processing in soil and ground water, contaminant hydrogeology, source tracing and characterization.
- Teaching: Stable Isotope Geology, Digital Simulation of Ground-Water Flow, Univ. of Arkansas/USGS Field Hydrogeology course, Field Geology, Engineering Geology.

July 1992 – July 2000, Hydrologist, U.S. Geological Survey, Little Rock, Arkansas. District Ground-Water Specialist:

- Provided expert technical advise to the District Chief in the areas of ground-water hydrology, water quality, surface-water/ground-water interaction, and contaminant hydrology;
- Supervision of technical component of all ground-water and contaminant hydrogeology related projects in the Arkansas District.

External Assignments:

U.S. Department of State, Embassy Science Fellow, Suriname Mercury and Gold Mining Pollution Abatement Program, January – April 2004.

- Designed and initiated a training program for new National environmental agency departments in Suriname (Geology and Mines Division of the Suriname Minerals Institute) and Guyana (Geology and Mines Commission);
- Worked as a technical liaison for the Guianas office of the World Wildlife Federation;

- Provided assistance on agency structure and mission definition for the new Suriname Geology and Mines Division Environmental Department;

Office of Ground Water, Defining water-resource issues and development of pilot and 10-year study plans for the President's Mississippi Delta Initiative, Mississippi Delta Region 2000 program, September 1999 – February 2000;

May 1989- September 1989, ARCO Geoscience Research Group, Research Geologist, Plano, Texas.

- Research geologist in the Geochemistry and Mineralogy Section investigating fluid flow and rock-water interaction and impact on contaminant transport and petroleum formation and migration.

June 1986 - September 1988, Sun Exploration and Production, Staff Geologist, Abilene, Texas.

- Petroleum geologist responsible for reserve development in central west Texas; developed drilling packages for, and drilled, 51 production wells.

Publications:

Van Brahana, Phillip D. Hays, Indrajeet Chaubey, Ralph Davis, John Murdoch, and Mohammed Al-Qinna, 2005, Quantification of Hydrologic Budget Parameters for the Vadose Zone and Epikarst in Mantled Karst, USGS Karst Interest Group Proceedings, 2005, USGS Scientific Investigations Report 2005-5160, p 144-153.

Sherri L. DeFauw, Thomas J. Sauer, Kristofer, R. Brye, Mary C. Savin, Phillip D. Hays, J. Van Brahana, 2005, Nitrate-N distributions and denitrification potential estimates for an agroforestry site in the Ozark Highlands, USA, World Agroforestry Congress, 7 p. Phillip D. Hays, 2004, Mercury Contamination in Suriname—A Legacy to Handicap a Generation: World Wildlife Federation Technical Publication SR-0405, 6 p.

Phillip D. Hays and Marie-Louise Felix, 2004, The Impact of Regional-Scale Mercury Contamination on the Animals of Suriname: World Wildlife Federation Technical Publication SR-0406, 8 p.

Phillip D. Hays and Beth B. Lampron, 2004, Mercury contamination and use in Suriname's gold mining industry: U.S. Department of State Political Cable Paramaribo 259, 10 p.

Phillip D. Hays and Richard W. Bell, in review, The Thermal Waters of Hot Springs National Park—Water Chemistry Status and Potential Water-Quality Effects of Cold-Water Recharge: U.S. Geological Survey Water Resources Investigation Report

Margaret Guccione, Phillip D. Hays, Erica Doerr, 2003, Use of stable isotopes in an alluvial environment to reconstruct Mississippi River watershed climate and local vegetation history near Lula, Mississippi, USA: Holocene, in review.

O'Neill, Brandy R., Walter L. Manger, Phillip D. Hays, 2003, Growth and Diagenesis of Middle Jurassic Belemnite Rostra from northeastern Utah, Insights using cathodoluminescence: Berliner Paläobiologische Abhandlungen, 12 pages, in press.

Phillip D. Hays, and P.W. McKee, 2003, The Sparta Aquifer: A sustainable regional resource?: U.S. Geological Survey Fact Sheet FS-111-02, 4 p.

Phillip D. Hays, J. Van Brahana, 2003, Observation Wells, in Encyclopedia of Hydrogeology, Sapna Maloor, ed., Marcel-Dekker, NYNY, at press.

John Van Brahana
Professor
Department of Geosciences
113 Ozark Hall, 479.575.2570, brahana@uark.edu

Education/Training

University of Missouri, Ph. D.-12/73 Geology/Hydrogeology, 9/68-6/71; University of Missouri, M.A., 6/68, Geology, 9/66-8/68; University of Illinois, A. B. 6/65 Arts and Sciences (Geology), 9/61-6/65.

Positions and Employment

- 1999-present: Professor, Dept. of Geosciences, U. of Arkansas, Fayetteville, AR.
- 1999-present: Scientist Emeritus, U.S. Geological Survey, Fayetteville, AR.
- 1990-1999: Adjunct Professor, Dept. of Geology, U. of Arkansas, Fayetteville, AR.
- 1990-1999: Research Hydrologist, U.S. Geological Survey, Fayetteville, AR.
- 1988-1990: Research Hydrologist, U.S. Geological Survey, Nashville, TN
- 1976-1988: Adjunct Professor, Geology, Vanderbilt Univ., Nashville, TN.
- 1975 Adjunct Professor, Univ. of Southern Mississippi (Univ. Center), Jackson, MS
- 1971-1988: Hydrologist, U.S. Geological Survey, Nashville, TN, Jackson, MS, and Denver, CO.

Professional Memberships and Experiences (Last 7 Years)

Geological Society of America (Fellow), American Geophysical Union, American Institute of Professional Geologists, International Association of Hydrogeologists, National Ground Water Association, National Speleological Society, International Mine Water Association, National Association of Geology Teachers.

Honors (Last 7 Years)

- Baum Teaching Grant Award--University of Arkansas 2002
- Scientist Emeritus -- U.S. Geological Survey 1999
- STAR Award – U.S. Geological Survey 1998

Courses Taught (Last 7 Years)

- (GEOS 4563H) Honors Geology of Our National Parks, Fayetteville, Spring Semester, 2003-present;
- (GEOS 4693) Environmental Justice, Fayetteville, Spring Semester alternate years, 2003-present;
- (GEOL Engineering Geology, Fayetteville, Fall Semester 2001 through 2004;
- (GEOL 3666) Field Geology. University of Arkansas, Dillon, Montana, Summer Semester 2001-present;
- (GEOL 1113) General Geology. Fayetteville, Fall Semester 2000 through 2002;
- (GEOL 4153) Karst Hydrogeology, Fayetteville, Fall Semester 1996 through present.
- (GEOL 5076) Field Hydrogeology, Fayetteville, Summer Semester 1994 through present, alternate years since 2000;
- (GEOL 4033) Hydrogeology, Fayetteville, Spring Semester 1991 through present.

Selected Peer-Reviewed Publications

Brahana, J.V., Hays, P.D., Al-Qinna, Mohammed, Murdoch, John F., Davis, Ralph K., Killingbeck, Jonathan J., Szilvagy, Eva, Doheny-Skubic, Margaret, Chaubey, Indrajeet, Ting, Tiong Ee, and Thoma, G., 2005, Quantification of hydrologic budget parameters for the vadose zone and epikarst in mantled karst: *in* Kuniandy, E.L., 2005, U.S. Geological Survey Karst

- Interest Group proceedings, Rapid City, South Dakota, September 12-15, 2005: U.S. Geological Survey Scientific Investigations Report 2005-5160, p. 144-152.
- Sauer, T.J., Logsdon, S.D., Brahana, J.V., and Murdoch, J.F., 2005, Variation in infiltration with landscape position: Implications for forest productivity and surface water quality: *Forest Ecology and Management*, v. 220, issues 1-3, p. 118-127.
- Davis, Ralph K., Hamilton, S., and Brahana, J.V., 2005, Survival of *Escherichia coli* in spring and stream sediments within the mantled karst of Northwest Arkansas: *Journal of the American Water Resources Association (JAWRA Paper No. 03134)* [in press, publication scheduled 2005].
- Hobza, Christopher M., Moffit, David C., Goodwin, Danny P., Kresse, Timothy, Fazio, John, Brahana, J.V., and Hays, Phillip D., 2005, Ground-water quality near a swine waste lagoon in a mantled karst terrane in northwestern Arkansas: *in* Kuniarsky, E.L., 2005, U.S. Geological Survey Karst Interest Group proceedings, Rapid City, South Dakota, September 12-15, 2005: U.S. Geological Survey Scientific Investigations Report 2005-5160, p. 155-162.
- Varnel, C.J., and Brahana, J.V., and Steele, K.F., 2004, The influence of coal quality variation on utilization of water from abandoned coal mines as a municipal water source: *Mine Water and the Environment*, v. 23, no. 4, p. 204-208.
- Brahana, J.V., 2003, Karst aquifers: *in* Stewart, B.A., and Howell, Terry, eds., *The Encyclopedia of Water Science*: Marcel Dekker, Inc., New York, p. 37-40.
- Brahana, J.V., 2003, Water quality in karst aquifers: *in* Stewart, B.A., and Howell, Terry, eds., *The Encyclopedia of Water Science*: Marcel Dekker, Inc., New York, p.41-42.
- Brahana, J.V., 2003, The Hydrologic cycle: *in* Stewart, B.A., and Howell, Terry, eds., *The Encyclopedia of Water Science*: Marcel Dekker, Inc., New York, p. 412-414
- Hays, P.D., and Brahana, J.V., 2003, Ground water observation wells: *in* Stewart, B.A., and Howell, Terry, eds., *The Encyclopedia of Water Science*: Marcel Dekker, Inc., New York., p. 633-635.
- Varnel, C.J., and Brahana, J.V., 2003, Neuse River-Impact of Animal Production on Water Quality: *in* Stewart, B.A., and Howell, Terry, eds., *The Encyclopedia of Water Science*: Marcel Dekker, Inc., New York, p.622-624.
- Peterson, E.W., Davis, R.K., Brahana, J.V., and Orndorff, H.O., 2002, Movement of nitrate through regolith covered karst terrane, northwest Arkansas: *Journal of Hydrology*, v. 256, p. 35-47.
- Steele, K.F., Davis, R.K., Brahana, J.V., Godfrey, Lyle, and Tatom, Ginger, 2002, Research and regulatory water-quality perspectives, Ozark Mountain Region, Arkansas: American Water Resources Association, *Ground Water/Surface Water Interactions*, p. 199-204
- Davis, R.K., Brahana, J.V., and Johnston, 2000, Ground water in northwest Arkansas: Minimizing nutrient contamination from non-point sources in karst terrane: Arkansas Water Resources Center, University of Arkansas, Fayetteville, 59 p.
- Peterson, E.W., Davis, R.K., and Brahana, J.V., 2000, The use of regression analysis to predict nitrate-nitrogen in springs in northwest Arkansas: *in* Sasowsky, I.D. and Wicks, C.M., editors, *Groundwater flow and contaminant transport in carbonate aquifers*: A.A. Balkema, Rotterdam, p. 43-63.
- Sauer, T.J., Alexander, R.B., Brahana, J.V., and Smith, R.A., 2001, The importance and role of watersheds in the transport of nitrogen: *in* Follett, R.F., and Hatfield, J.L., eds., *Nitrogen in the Environment: Sources, Problems, and Management*: ch. 7, p. 147-181.