



Special Publication 19

# Karst Groundwater Contamination and Public Health

Edited by  
**William B. White**  
**Ellen K. Herman**  
**Marian Rutigliano**  
**Janet S. Herman**  
**Dorothy J. Vesper**  
**Scott A. Engel**



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# Karst Groundwater Contamination and Public Health

# 2016

Abstracts and Field Trip Guidebook for the  
Symposium held January 27 through 30, 2016,  
San Juan, Puerto Rico

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**William B. White**  
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Cover caption: Cone and tower karst near Arecibo, Puerto Rico  
Photo credit: William B. White



**KARST GROUNDWATER CONTAMINATION AND PUBLIC HEALTH  
JANUARY 27-30, 2016  
San Juan, Puerto Rico**

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## PREFACE

**E**nvironmental contamination is an issue worldwide and impacts public health, ecosystems, and resource availability. The introduction, fate, and transport of contaminants into the environment, and specifically into groundwater, has been a focus of a great deal of research. Most investigations have focused on granular (porous) and fractured aquifers. Far less attention has been paid to the contamination of karst aquifers.

Case studies have demonstrated that the movement of contaminants in karst aquifers is poorly, if at all, predictable. On one hand, contaminants may travel rapidly through the aquifer due to direct input, open pathways, and high flow velocities. In contrast, under other conditions, contaminants may be stored in the aquifer for long periods of time and gradually released at low concentrations. There have been a substantial number of studies of the movement of specific contaminants in specific aquifer locations – case studies – but much less consideration of more generalized concepts of contaminant injection, storage, transmission, and release. More importantly, much less attention has been given to the actual impact of contaminated karst aquifers on public health. Given the importance of karst aquifers as water resources worldwide, it behooves us to consider (1) how contaminant movement differs in karst aquifers and (2) what is the consequent threat to people who use these waters?

This conference was convened in San Juan, Puerto Rico, to provide a comprehensive overview of groundwater contamination in karst aquifers and its impact on public health. The Puerto Rico karst is especially significant in that it provides drinking water for private residences and for municipal water supplies and, at the same time, has been significantly impacted by unlined landfills and industrial contamination. Speakers were invited to present current research findings while providing the broadest possible topical coverage and including the widest possible range of points of view.

The program was arranged with keynote and invited speakers plus contributed oral and poster papers. A session of snap talks was held for those who wished to make short or last-minute reports. Abstracts for all presentations except the snap talks are given in the following pages. The presentations have been arranged to present the tools available to investigators for assessing contamination problems, transport and remediation for specific contaminants, exposure concentrations, impacts on human health, and the regulatory framework.

Two field trips gave attendees direct acquaintance with the Puerto Rico karst and its environmental problems. The mid-conference trip visited the San Juan Estuary. A two day field trip through the karst of the north coast followed the conference for attendees to see the spectacular cone and tower karst of Puerto Rico and a few of its caves and to gain some insight into the often hidden threats to the groundwater that flows beneath the dramatic landscape.

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# TECHNICAL PROGRAM

**Wednesday January 27, 2016 – Evening session 6:30 pm – 9:30 pm**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
<b>Opening Session</b>	
6:30 pm	Opening Reception
7:30 pm	Welcoming Session
	Welcome by President of the Karst Waters Institute <b>Janet S. Herman</b> University of Virginia
	Welcome by Conference Chair <b>Dorothy J. Vesper</b> West Virginia University
	Welcome by Local Host <b>Ingrid Y. Padilla</b> University of Puerto Rico-Mayagüez
	Welcome by National Institutes of Health-National Institute of Environmental Health Sciences <b>Heather Henry</b> National Institute of Environmental Health Sciences
8:15 pm	<b><u>Keynote Lecture:</u></b> The Puerto Rico test site for exploring contamination threats (PROTECT) and the intersection of karst and public health science <b>José F. Cordero<sup>1</sup></b> and Akram Alshawabkeh <sup>2</sup> <sup>1</sup> University of Georgia; <sup>2</sup> Northeastern University

**Thursday January 28, 2016 – Morning session 8:30 am – 11:40am**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
8:30 am	Orientation to the day's presentations <b>Technical Program Committee</b>
<b>Current state of knowledge in karst contaminant transport</b>	
8:40 am	<b>Keynote Lecture:</b> Contaminant transport in karst aquifers: Systematics and mechanisms? <b>William B. White</b> The Pennsylvania State University
9:10am	<b>Keynote Lecture :</b> Fate, transport, and exposure of emerging and legacy contaminants in karst systems: State of knowledge and uncertainty <b>Ingrid Y. Padilla<sup>1</sup>, William B. White<sup>2</sup>, and Dorothy J. Vesper<sup>3</sup></b> <sup>1</sup> University of Puerto Rico-Mayagüez; <sup>2</sup> The Pennsylvania State University; <sup>3</sup> West Virginia University
<b>Contaminants and tools for investigating contaminant transport</b>	
9:40 am	Quantification of wastewater infiltration and transport processes in karst aquifers <b>Martin Sauter</b> , Sebastian Schmidt, Olav Hillebrand, Karsten Nödler, and Tobias Licha Georg-August-Universität Göttingen
10:00 am	<b>Coffee Break</b>
10:20 am	Microbial contamination in karst: From monitoring to process comprehension <b>Michael Sinreich</b> Swiss Federal Office for the Environment
10:40 am	Comparative study of specific groundwater vulnerability of a karst aquifer in Central Florida <b>Philip E. van Beynen<sup>1</sup>, Michael Niedzielski<sup>2</sup>, Elzbieta Bialkowska-Jelinska<sup>1</sup>, and Kamal Alsharif<sup>1</sup></b> <sup>1</sup> University of South Florida; <sup>2</sup> University of North Dakota
11:00 am	Mobility of <i>Escherichia coli</i> compared to traditional groundwater tracers within karst terrains <b>Ashley Bandy<sup>1</sup>, Alan Fryar<sup>1</sup>, Kim Cook<sup>2</sup>, Jason Polk<sup>3</sup>, Kegan McClanahan<sup>3</sup>, and Stephen Macko<sup>4</sup></b> <sup>1</sup> University of Kentucky; <sup>2</sup> U.S. Department of Agriculture-Agricultural Research Service; <sup>3</sup> Western Kentucky University; <sup>4</sup> University of Virginia
11:20 am	Selected micropollutants as indicators in a karst catchment <b>Johannes Zirlewagen<sup>1</sup>, Ferry Schiperski<sup>1</sup>, Olav Hillebrand<sup>2</sup>, Karsten Nödler<sup>3</sup>, Tobias Licha<sup>2</sup>, and Traugott Scheytt<sup>1</sup></b> <sup>1</sup> Technische Universität Berlin; <sup>2</sup> University of Göttingen; <sup>3</sup> Water Technology Center Karlsruhe
11:40 am	<b>Lunch on your own</b>



**Thursday January 28, 2016 – Afternoon session 1:30 pm – 6:00 pm**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
<b>Contaminants and tools for investigating contaminant transport (continued)</b>	
1:30 pm	<b>Summary of morning talks &amp; discussion</b> Technical Program Committee
1:50 pm	Relationship between organic micropollutants and hydro-sedimentary processes at a karst spring in southwest Germany <b>Ferry Schipperski<sup>1</sup></b> , Johannes Zirlewagen <sup>1</sup> , Olav Hillebrand <sup>2</sup> , Karsten Nödler <sup>2,3</sup> , Tobias Licha <sup>2</sup> , and Traugott Scheytt <sup>1</sup> <sup>1</sup> Technische Universität Berlin; <sup>2</sup> University of Göttingen; <sup>3</sup> Water Technology Center Karlsruhe
2:10 pm	Integrated strategy to guide microbial quality management at alpine karst water resources: Part I – Hydrogeological investigations to elucidate fecal pollution dynamics <b>Hermann Stadler<sup>1</sup></b> , Regina Sommer <sup>2</sup> , Wolfgang Zerobin <sup>3</sup> , and Andreas H. Farnleitner <sup>4</sup> <sup>1</sup> Joanneum Research; <sup>2</sup> Medical University of Vienna; <sup>3</sup> Vienna Water; <sup>4</sup> Technische Universität Wien
2:30 pm	Integrated strategy to guide microbial quality management at alpine karst water resources: Part II – Towards fecal hazard characterization and risk management <b>Andreas H. Farnleitner<sup>1</sup></b> , Regina Sommer <sup>2</sup> , Georg Reischer <sup>1</sup> , Alexander Kirschner <sup>2</sup> , Wolfgang Zerobin <sup>3</sup> , and Hermann Stadler <sup>4</sup> <sup>1</sup> Technische Universität Wien; <sup>2</sup> Medical University of Vienna; <sup>3</sup> Vienna Water; <sup>4</sup> Joanneum Research
2:50 pm	Trace metal accumulation and cycling in phreatic karst conduits <b>Amy L. Brown</b> , Jonathan B. Martin, George Kamenov, and Elizabeth Sreaton University of Florida
3:10 pm	<b>Coffee break</b>
3:30 pm	Natural and enhanced bioremediation of contaminants in karst aquifers <b>Thomas Byl<sup>1,2</sup></b> , Michael Bradley <sup>1</sup> , and Roger Painter <sup>2</sup> <sup>1</sup> U.S. Geological Survey-Water Science Center; <sup>2</sup> Tennessee State University
3:50 pm	Development of the electrochemical technologies for remediation of contaminated groundwater <b>Ljiljana Rajic</b> , Noushin Fallahpour, Roya Nazari, and Akram Alshawabkeh Northeastern University
4:10 pm	Investigating and remediating contaminated karst aquifers <b>Malcolm S. Field<sup>1</sup></b> and Neven Kresic <sup>2</sup> <sup>1</sup> U.S. Environmental Protection Agency; <sup>2</sup> Amec Foster Wheeler Americas
4:30 pm	Discussion and day summation <b>Technical Program Committee</b>
5:00 pm	<b>Snap talks</b>
7:00pm	<b>Dinner on your own</b>



**Friday January 29, 2016 – Morning session 8:30 am – 11:45am**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
8:30 am	Orientation to the day's presentations <b>Technical Program Committee</b>
<b>Exposure concentrations and human health</b>	
8:40 am	Factors influencing the occurrence and the fate of <i>E. coli</i> population in karst hydrosystem <b>Fabienne Petit</b> <sup>1</sup> , Thierry Berthe <sup>1</sup> , Erick Denamur <sup>2</sup> , Olivier Clermont <sup>2</sup> , Nicolas Massei <sup>1</sup> , Jean-Paul Dupont <sup>1</sup> , Philip C. Bennett <sup>3</sup> , Manon Michaud <sup>1</sup> , and Gautier Chaix <sup>1</sup> <sup>1</sup> Normandie Université; <sup>2</sup> Université Paris Diderot; <sup>3</sup> University of Texas
9:00 am	Using enteric pathogens to assess sources of fecal contamination in the Silurian dolomite aquifer: Preliminary results <b>Maureen A. Muldoon</b> <sup>1</sup> , Mark A. Borchardt <sup>2</sup> , Susan K. Spencer <sup>2</sup> , Laura Hubbard <sup>3</sup> , and Randall J. Hunt <sup>3</sup> <sup>1</sup> University of Wisconsin-Oshkosh; <sup>2</sup> U.S. Department of Agriculture-Agricultural Research Service; <sup>3</sup> U.S. Geological Survey-Wisconsin Water Science Center
9:20 am	Potential exposure of emerging contaminants in karst groundwater through tapwater sources <b>Norma I. Torres Torres</b> , Ingrid Y. Padilla, and Vilda L. Rivera University of Puerto Rico-Mayagüez
9:40 am	Environmental exposures among pregnant women in the northern karst region of Puerto Rico <b>John Meeker</b> University of Michigan
10:00 am	<b>Coffee Break</b>
10:20 am	<b>Keynote Lecture:</b> Cholera and climate: The Haiti experience <b>Rita R. Colwell</b> University of Maryland
11:20 am	Discussion – Integrating geology and human health <b>Technical Program Committee</b>
11:50 am	<b>Lunch on your own</b>



**Friday January 29, 2016 – Afternoon session 1:00 pm – 7:00 pm**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
<b>Exposure concentrations and human health (continued)</b>	
1:00 pm	<b>Summary of morning talks &amp; discussion</b> Technical Program Committee
1:10 pm	<b>Keynote Lecture:</b> Beyond case reports: Placing karst in context in public health response to groundwater contamination <b>Marian Rutigliano</b> U.S. Environmental Protection Agency
1:40pm	Spatiotemporal assessment of CVOC contamination in karst groundwater sources and exposure at tap water point of use <b>Vilda L. Rivera</b> , Ingrid Y. Padilla, and Norma I. Torres University of Puerto Rico-Mayagüez
2:00 pm	Social determinants of contaminant exposure and maternal and child health in the northern karst of Puerto Rico <b>Nancy Cardona</b> <sup>1</sup> , Carmen M. Vélez Vega <sup>1</sup> , José Cordero <sup>2</sup> , Colleen Murphy <sup>1</sup> , Carlos Vergara <sup>1</sup> , John Meeker <sup>3</sup> , Akram Alshawabkeh <sup>4</sup> , and Liza Anzalota <sup>1</sup> <sup>1</sup> University of Puerto Rico-Medical Sciences Campus; <sup>2</sup> University of Georgia; <sup>3</sup> University of Michigan; <sup>4</sup> Northeastern University
2:20 pm	Phytoforensics: Using plants as biosentinels of in-home exposure pathways <b>Joel G. Burken</b> Missouri University of Science and Technology
2:40 pm	<b>Coffee break</b>
3:00 pm	Moving beyond case studies: Research examples from mountaintop removal coal mining <b>Michael Hendryx</b> Indiana University
3:20 pm	Frameworks for protecting public health in the context of surface water recreation: Implications for karst research <b>Samuel Dorevitch</b> University of Illinois-Chicago
3:40 pm	Discussion and day summation <b>Technical Program Committee</b>
4:00 pm	<b>Poster session &amp; reception</b>
7:00pm	<b>Dinner on your own</b>

**Saturday January 30, 2016 – Morning session 8:30 am – noon**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
8:30 am	Orientation to the day’s presentations, poster discussion <b>Technical Program Committee</b>
<b>Orientation to the geology and hydrology of Puerto Rico</b>	
9:00 am	<b><i>Keynote Lecture:</i></b> The karst regions of Puerto Rico <b>Thomas Miller</b> University of Puerto Rico-Mayagüez
10:00 am	<b><i>Coffee break</i></b>
<b>Regulatory issues in karst water resources</b>	
10:20 am	Protecting the karstic corner: A challenge to Minnesota’s drinking water <b>James L. Berglund<sup>1</sup></b> , Justin L. Blum <sup>2</sup> , and Emily Berquist <sup>2</sup> <sup>1</sup> Temple University; <sup>2</sup> Minnesota Department of Health
10:40 am	Karst – Fitting regulatory square pegs into round holes <b>Jesse J. Richardson, Jr.</b> West Virginia University
11:00 am	On the implementation of environmental indices in karst Marianna Mazzei <sup>1</sup> and <b>Mario Parise<sup>2</sup></b> <sup>1</sup> Salento University; <sup>2</sup> National Research Council-Research Institute for Hydrogeological Protection
11:20 am	Addressing hazardous materials releases in karst terrains <b>Geary M. Schindel</b> Edwards Aquifer Authority
11:40 am	Discussion and technical program summation <b>Technical Program Committee</b>
Noon	<b><i>Lunch on your own</i></b>

**Saturday January 30, 2016 – Afternoon session 1:00 pm – 5:00 pm**

<i>Start time</i>	
<b>Field trip to community environmental project focused on San Juan Bay Estuary</b>	
1:00 pm	Introduction to the San Juan Bay Estuary System
2:00 pm	Field trip to community environmental project departs
5:00 pm	Field trip returns to conference hotel



**Saturday January 30, 2016 – Evening session 7:00 – 10:00 pm**

<i>Start time</i>	<i>Title, Author, Affiliation</i>
<b>Closing banquet and awards ceremony</b>	
7:00 pm	Closing banquet
8:00 pm	Concluding remarks by Conference Chair <b>Dorothy J. Vesper</b> West Virginia University
	Concluding remarks by Local Host <b>Ingrid Y. Padilla</b> University of Puerto Rico-Mayagüez
	Concluding remarks from Chair of the Board of Directors, KWI <b>Jack Hess</b> Geological Society of America Foundation
	Presentation of KWI Karst Award for 2016 by President, KWI <b>Janet S. Herman</b> University of Virginia
8:30 pm	<b><u>Award Lecture:</u></b> Puerto Rico's karst protection – Beyond the law and regulations <b>Abel Vale Nieves</b> Ciudadanos Del Karso

**Posters – Friday January 29, 2016 – 4:00 pm – 7:00 pm**

<i>Poster #</i>	<i>Title, Author, Affiliation</i>
1	Cave characterization in the north coast karst belt zone of Puerto Rico <b>Ángel A. Acosta-Colón</b> University of Puerto Rico-Arecibo
2	Bassett’s Cave Bermuda <b>Maureen Handler</b> and John Hoffelt Southern Environmental Technologies
3	Improving the karst groundwater catchment area isohyet map of Río Tanamá, Arecibo Puerto Rico, using a geographic information system software method <b>Orializ Martínez Román</b> and Thomas E. Miller University of Puerto Rico-Mayagüez
4	Development and testing of hydrogel beads as potential tracers of contaminant movement in karst aquifers <b>Dorothy J. Vesper</b> <sup>1</sup> , Amanda F. Laskoskie <sup>2</sup> , Habib Bravo-Ruiz <sup>1</sup> , and Harry M. Edenborn <sup>3</sup> <sup>1</sup> West Virginia University; <sup>2</sup> Weston Solutions; <sup>3</sup> National Energy Technology Laboratory
5	Assessment of flow and transport properties in an intermediate karstified lab-scale physical model using hydraulic and tracer response analysis <b>Jonathan Toro-Vázquez</b> and Ingrid Y. Padilla University of Puerto Rico-Mayagüez
6	Clastic sediments in karst as a vehicle for contaminant transport: Lithofacies and transport mechanisms <b>Rachel Bosch</b> and William B. White The Pennsylvania State University
7	Delineation of a major karst spring basin with multiple input points, Roaring River, Tennessee <b>Ryan Gardner</b> , Evan Hart, Steve Anderson, Sid Jones, Chuck Sutherland, and Joseph Asante Tennessee Technological University
8	Water tracing tests and public health in karst areas <b>William K. Jones</b> Karst Waters Institute
9	Quantitative dye studies to evaluate the spill response system for Mammoth Cave National Park <b>JeTara Brown</b> <sup>1</sup> , Rickard Toomey, III <sup>2</sup> , and Lonnie Sharpe, Jr. <sup>1</sup> <sup>1</sup> Tennessee State University; <sup>2</sup> Mammoth Cave National Park
10	Stormwater runoff characterization and treatment system efficiency analysis in Mammoth Cave National Park <b>Hung-Wai Ho</b> <sup>1</sup> , David Solomon <sup>1</sup> , and Rick Toomey <sup>2</sup> <sup>1</sup> Tennessee State University; <sup>2</sup> Mammoth Cave National Park



11	Anthropogenic nutrient loading on an epigenic karst aquifer in Southeastern Kentucky <b>Gilles V. Tagne</b> and Lee J. Florea Ball State University
12	Current state of metal toxicity and remediation in the Tri-State Mining District, USA Aaron W. Johnson <sup>1</sup> , <b>Douglas R. Gouzie</b> <sup>2</sup> , Melida Gutierrez <sup>2</sup> , and L. Rex Mcaliley <sup>1</sup> <sup>1</sup> Northwest Missouri State University; <sup>2</sup> Missouri State University
13	Where is the greatest potential for superficial contamination in the North Coast Limestone aquifer of Puerto Rico? <b>Ronald T. Richards</b> <sup>1</sup> , Anastacio Emiliano <sup>1</sup> , and Rafael Méndez-Tejeda <sup>2</sup> <sup>1</sup> Universidad del Turabo; <sup>2</sup> University of Puerto Rico-Carolina
14	Recharge and water-quality controls for a karst aquifer in central Texas <b>Brian A. Smith</b> and Brian B. Hunt Barton Springs/Edwards Aquifer Conservation District
15	Cave monitoring results from Cueva Larga, Puerto Rico <b>Rolf Vieten</b> <sup>1</sup> , Amos Winter <sup>1</sup> , Thomas Miller <sup>1</sup> , Andrea Schroeder-Ritzrau <sup>2</sup> , Sophie Winterhalder <sup>2</sup> , and Christoph Spötl <sup>3</sup> <sup>1</sup> University of Puerto Rico-Mayagüez; <sup>2</sup> University of Heidelberg; <sup>3</sup> Leopold-Franzens-Universität Innsbruck
16	Cave conduits as receptacles of trash and septic tank contamination of karst in Puerto Rico <b>Thomas Miller</b> University of Puerto Rico-Mayagüez
17	Hydrologic analysis of a poplar-based phytoremediation system <b>Felix L. Santiago Collazo</b> <sup>1</sup> , Alan J. Rabideau <sup>2</sup> , and Beynan Ransom <sup>2</sup> <sup>1</sup> University of Puerto Rico-Mayagüez; <sup>2</sup> State University of New York at Buffalo
18	Tennessee cave life relational geodatabase <b>Chuck Sutherland</b> Tennessee Technological University

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## ABSTRACTS



# CAVE CHARACTERIZATION IN THE NORTH COAST KARST BELT ZONE OF PUERTO RICO

*Ángel A. Acosta-Colón*

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To completely understand a cave system, we have to characterize the geological, geometrical, physicochemical and biological properties and study the relationship between them. The geological properties provide us with information for the speleogenesis of the cave; this can be found from a literature review of the region. The geometrical properties consisted of the cartography of the cave in which the path, area and volume can be calculated using caveGEOmap and lidar measurements. The geometrical measurements were collected by using a laser digital distance measurer, clinometer, and a compass to create 2-D and 3-D maps of the cave. These can be used as a reference for the other properties that were measured. For our study the geophysicochemical properties consisted on the chemical composition and properties of bat guano droppings that can be used to understand the mycological settings for guanophilic fungi and mesofauna. The geobiological properties were the characterization of the fauna of the cave by catch-and-release traps. For the traps, the specimens were collected and classified by biological orders as a function of the depth of the cave. Based on these properties we can study the cave's possible health impacts to humans such as water transport of bacteria, fecal coliforms, histoplasmosis, and others. At this conference we will present the results of two case studies; Angel Matos and Efrain Lopez located in the municipalities of Arecibo and Isabela, respectively.

# CLASTIC SEDIMENTS IN KARST AS A VEHICLE FOR CONTAMINANT TRANSPORT: LITHOFACIES AND TRANSPORT MECHANISMS

*Rachel Bosch<sup>1\*</sup> and William B. White<sup>2</sup>*

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**K**arstic aquifers carry a load of clastic sediment as part of their hydrologic function. Clastic sediments are an important part of the mechanism for storage and transport of contaminants; indeed, solid contaminants can be considered as a form of clastic sediment. Although the sources of clastic sediments have been well delineated, sediments from multiple sources are mixed and redistributed within the aquifer to produce the sediment deposits observed in caves or the load of sediment discharged from karst springs. As an aid to the interpretation of clastic sediments in karst aquifers, a facies concept has been devised based on the traditional criteria of sedimentary petrology. Facies are defined in terms of particle size, degree of sorting, and sedimentary structures. The deposits represented by each set of facies characteristics in turn can be interpreted in terms of depositional mechanisms. The facies interpreted as slackwater cave deposits, here referred to as *slackwater facies*, are laminated deposits of clay to silt laid down in passages filled with stagnant water either flooded by inputs from upstream or backflooded from surface streams. This mechanism provides two pathways by which microorganisms or metals can be adsorbed onto clay particles and carried into the aquifer. The facies interpreted as channel cave deposits, here referred to as *channel facies*, consist of silts, sands, gravels, and cobbles carried in major conduits mostly by high velocity storm flows. Flows that transport sediments resulting in channel facies also can carry solid contaminants at various size scales and can act as storage sites for contaminants over long periods of time. Calculations show that hydraulic conditions required for transport leading to deposition of channel facies are consistent with observed discharge characteristics of major conduits.

# MOBILITY OF *ESCHERICHIA COLI* COMPARED TO TRADITIONAL GROUNDWATER TRACERS WITHIN KARST TERRAINS

Ashley Bandy<sup>1\*</sup>, Alan Fryar<sup>1</sup>, Kim Cook<sup>2</sup>, Jason Polk<sup>3</sup>, Kegan McClanahan<sup>3</sup>, and Stephen Macko<sup>4</sup>

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An understanding of fundamental processes controlling pathogen movement is necessary to protect water resources across the globe. Limited filtration and turbulent flow make karst aquifers susceptible to microbial contamination. Groundwater tracers typically used in karst terrains include fluorescent dyes and latex microspheres. Not only can these tracers be cost-prohibitive, depending on the system being studied, but they may not accurately mimic the transport behaviors of bacteria and other potential pathogens, and thus may not be good proxies for risk assessment involving microorganisms. This study examines the movement and attenuation of two serotypes of *Escherichia coli* (*E. coli*) with differing attachment efficiencies compared to traditional tracers (rhodamine WT dye and 1- $\mu$ m diameter fluorescent microspheres). *E. coli* is quantified by molecular methods (qPCR) and dual stable isotope analyses using enrichment levels of <sup>13</sup>C and <sup>15</sup>N. Transport of the tracers is being evaluated for (1) vertical infiltration through the epikarst above Crumps Cave near Smiths Grove, KY following storms and (2) lateral flow within a karst conduit aquifer near Lexington, KY under baseflow conditions. Breakthrough curves show differential behavior among all of the tracers within the epikarst, with the isolate containing the *iha* gene having later breakthrough curves than the isolate with the *kps* gene. Field data on survival and transport of agricultural isolates of *E. coli* can be applied to improve transport models and used by regulatory agencies for making decisions to mitigate bacterial contamination of water resources in karst terrains.

# PROTECTING THE KARSTIC CORNER: A CHALLENGE TO MINNESOTA'S DRINKING WATER

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The Minnesota Department of Health is delegated to protecting the state's drinking water resources. One challenging area is the thinly-mantled karstic Paleozoic plateau in the southeast which, in contrast to the rest of the state, does not have a cover of thick glacial sediments left over from the last Ice Age. In this region, it is often a struggle for drinking water protection to strike a balance between well-defined regulatory policy and the hydrologic uncertainty associated with karst systems. As the distinction between surface water and groundwater becomes poorly defined, potable groundwater sources within the state become more susceptible to surface contaminants, such as nitrates from increasing agricultural activities and animal waste from feedlots. The dynamic nature of sinkhole formation also creates contamination hazards, such as the collapsing of sewage lagoons. Issues such as these have necessitated the development of practices and regulations unique to karst. Through drinking water monitoring programs, wellhead protection plans, and well construction guidelines, the Minnesota Department of Health aims to protect these drinking water sources in the state's karstic corner.

# TRACE METAL ACCUMULATION AND CYCLING IN PHREATIC KARST CONDUITS

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Little is known about how trace metals accumulate and cycle in conduits within the phreatic zone. These water-filled conduits can receive flood water that allows metals to accumulate, similar to air-filled caves, but are more susceptible to reducing conditions following floods because oxygen is limited to dissolved concentrations. If sufficient reactive organic carbon is transported into the aquifer, oxygen consumption will lower Eh and mobilize manganese and iron. To evaluate this accumulation and mobilization of metals, we analyzed the geochemical and isotopic composition of water, solid metal oxide, and limestone samples from two phreatic systems in north-central Florida where river water displaces aquifer water following storms. River water was a net source of trace metals to the aquifer; however, manganese depletion in the interior of the metal oxides relative to concentrations in intruding river water indicates not all metals are retained in the aquifer as redox conditions changed. The metal oxides are actively incorporating metals from floods, with anthropogenically-sourced lead from surface water on the outer portion of the metal oxide. Strontium isotopes indicate metal oxides form after river intrusion from a mixture of river and spring water, which have distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Isotopic and geochemical evidence indicate that there is net accumulation of metal oxides in the aquifer, but not all accumulated metals are permanently sequestered. Understanding the conditions that trigger metal sequestration and remobilization is critical to managing water quality.

# QUANTITATIVE DYE STUDIES TO EVALUATE THE SPILL RESPONSE SYSTEM FOR MAMMOTH CAVE NATIONAL PARK

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**M**ammoth Cave National Park in south-central Kentucky, an International Biosphere Reserve since 1990, is the world's largest cave with over 400 miles of passages and a cave ecosystem that is linked to the surface through groundwater recharge. Groundwater quality in the Mammoth Cave region of Kentucky is critical to the cave's ecosystem, tourism, and the health of the Green River. However, the same hydrogeologic processes that formed the cave make the karst system vulnerable to contamination. Many of the natural storm-drainage flowpaths go directly to sinkholes. It is well known that preventing contamination of the groundwater is preferable to remediation. Therefore, the objective of this study was to measure the effectiveness of temporary check dams used to impede transport from a surface sewer leak into the cave. Three quantitative tracer studies were conducted in 2014-15 to test the effectiveness of the check dams. The presence and absence of two temporary check dams constructed with pea-gravel were the main variables in the studies. The dams increased mean residence time on the surface from approximately 2 to 16 hours, providing management more time to implement waste recovery. The dams also reduced the quantity of dye entering the cave by 90%. Temporary check dams provide emergency responders with an effective way to impede contaminants from entering the karst groundwater system at Mammoth Cave National Park.



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# PHYTOFORENSICS: USING PLANTS AS BIOSENTINELS OF IN-HOME EXPOSURE PATHWAYS

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Plants interact intimately with their environment. Although stationary, plants are masters of mass transfer and extract water, nutrients, carbon, oxygen and all that is needed to be the dominant terrestrial, multicellular biomass on earth. Plants concurrently change their environment while collecting and storing chemicals and elements from the surrounding water, air, and soil in the environment, all by harnessing the energy of the sun and wind. Phytoforensics is an approach to gather this information using novel sampling and chemical analysis techniques developed at S&T, offering not just screening, but long-term monitoring possibilities. Fundamental breakthroughs in understanding plant-contaminant interactions have led to novel approaches that now being used in the new field of phytoforensics. Recent findings show a clear relationship of in-plant concentrations of volatile organic compounds and the potential for vapor intrusion into homes. Plants in the urban environment occupy the same environmental volume as homes and can therefore offer a quick, robust screening tool to test for potential in-home exposures. The time-weighted sampling that trees provide are not subject to the variability of in-home sampling and thereby provide reliable assessment of subsurface pollutants and an additional protective, cost effective protection of human health.

# NATURAL AND ENHANCED BIOREMEDIATION OF CONTAMINANTS IN KARST AQUIFERS

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The carbonate aquifers of central Tennessee and Kentucky are vulnerable to dissolved and non-aqueous phase contamination due to contaminant transport through sinkholes, fractures, and other karst features. The complexity of local karst hydrology often prevents the efficient removal of contaminants through the use of traditional pump-and-treat methods. Bioremediation, in some instances, is a viable remediation option, with suitable hydrological, geochemical and microbial site conditions. Tracer studies are essential for characterizing site hydrology and estimating residence times. Sample collection and evaluation of the geochemical conditions and existing bacterial types are critical as part of the site evaluation. Supplements have been used to stimulate specific microbial populations and foster geochemical conditions which enhance or stimulate degradation or immobilization of the contaminants in a karst aquifer. Bacteria indigenous to Tennessee and Kentucky karst systems are well adapted to a variety of metabolic capabilities and aquifer conditions. Non-traditional groundwater models that incorporate residence time distribution and decay rates are useful tools in the remediation decision-making process.

# SOCIAL DETERMINANTS OF CONTAMINANT EXPOSURE AND MATERNAL AND CHILD HEALTH IN THE NORTHERN KARST OF PUERTO RICO

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Socioeconomic inequalities of disease and health are a major issue in the development of public policy, specifically health policies. The study uses secondary data obtained from a subset of participants of the Puerto Rico Testsite for Examining Contamination Threats (PROTECT) project that follows a cohort of pregnant women and their exposure to contaminant agents. This study includes a profile of PROTECT participants by geographical region, study site, and other socioeconomic characteristics related to an increased risk of differential exposure to contaminants by means of use of personal care products. The analysis will include the study of socioeconomic and demographic variables, and the use of personal care products. The sample for this study consisted of those woman who participated in the completion of three questionnaires. Analysis of data collected reveals reports of use of products with higher concentrations of chemicals that have been associated with hormone disruption, and premature births, are not evenly distributed among the population participating in the study. The presentation will discuss the distribution of personal care product use and socioeconomic characteristics of the participants from diverse geographical sites in Puerto Rico. Results provide important evidence in terms of the social determinants of health such as geographical location, neighborhood, age, education, gender and economic resources, and how they impact exposure to chemicals present in personal care products. The implications of the results for further research, as well as for community engagement, and public policy will be discussed.

# CHOLERA AND CLIMATE: THE HAITI EXPERIENCE

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The millions of deaths from cholera during the past 200 years, coupled with the morbidity and mortality of cholera in Haiti since October, 2010, are reminders that *Vibrio cholerae*, the etiologic agent of cholera, remains a scourge. Based on work done on *V. cholerae* and related vibrios over the past 40 years and, more recently, in Haiti, we reported the isolation of both *V. cholerae* O1 and non-O1/O139 early in the Haiti cholera epidemic from samples collected from victims in 18 towns across eight Arrondissements of Haiti. The results showed two distinct populations of *V. cholerae* coexisted in Haiti early in the epidemic. As non-O1/O139 *V. cholerae* was the sole pathogen isolated from 21% of the clinical specimens, its role in this epidemic, either alone or in concert with *V. cholerae* O1 could not be dismissed. A combined climate analysis and genomic approach was used to examine the similarities and differences among the Haitian *V. cholerae* O1 and *V. cholerae* non-O1/O139 isolates from patients and the environment were sequenced and compared against more than 200 *Vibrio* sequences. Comparative genome analyses of *V. cholerae* isolated in concurrent epidemics outside Haiti and our *V. cholerae* genomes database demonstrated substantial diversity of *V. cholerae* and ongoing flux within its genome. Furthermore, historical analyses of climate variables strongly indicate an environmental driver in the Haiti epidemic.

# THE PUERTO RICO TESTSITE FOR EXPLORING CONTAMINATION THREATS (PROTECT) AND THE INTERSECTION OF KARST AND PUBLIC HEALTH SCIENCE

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**P**ROTECT is a transdisciplinary science program set at the intersection of engineering, biomedical, and earth sciences. Based in Puerto Rico, it is a research consortium led by Northeastern University, University of Michigan, and the University of Puerto Rico and its theme is preterm births, births occurring before completing 37 weeks of gestation. Puerto Rico has a long-standing history of preterm births, with the highest rate of any jurisdiction in the United States and third highest worldwide. Medical risk factors do not explain the high rate and Puerto Rico has the highest density per square mile of waste sites recognized by the US Environmental Protection Agency, most are located in the northern karst area, the selected study site for PROTECT. The core study for PROTECT centers on a prospective epidemiologic study of 1,800 pregnant women that examines the role of phthalates and other endocrine disruptors on preterm births. A unique aspect of this program is its intersection of geology, meteorology, and engineering with biomedical sciences. The research results of geologic studies in the northern karst area, are informing the epidemiologic analysis of this program and providing new insights on how contaminants diffuse and lead to exposures in humans. PROTECT is a strong model of transdisciplinary science that is advancing new knowledge that can be translated into a healthier environment and healthier people.

# FRAMEWORKS FOR PROTECTING PUBLIC HEALTH IN THE CONTEXT OF SURFACE WATER RECREATION: IMPLICATIONS FOR KARST RESEARCH

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Pathogenic microbes that contaminate karst groundwater have caused infectious disease outbreaks. The microbes responsible for these outbreaks have also caused disease in the setting of surface water recreation. To protect the health of the public at beaches, regulatory frameworks have been established, which involve water monitoring and public notification. These monitoring and notification programs 35 years ago involved culturing fecal indicator bacteria and summarizing water quality days or weeks after sample collection. Presently, the use of rapid molecular methods allow same-day notification about water quality, in some cases through social media or text messaging. In the context of research, not only are indicator microbes quantified, but likely sources of those organisms can be identified. Pathogen monitoring methods have been simplified in recent years and have been deployed in the field in studies of water and health. Additionally, a surveillance system tracks waterborne disease outbreaks that have been identified by local and state health departments.

In this presentation, the potential relevance of the above approaches to karst groundwater is described. The potential advantages and disadvantages of performing karst monitoring for public health purposes will be addressed. Critical information needed to inform the design of such a monitoring and notification system will be described. Locations for such monitoring could be prioritized based on demographic, population health, pollutant source, hydrologic, and other factors. Leveraging existing karst groundwater sampling activities so that infectious agents can be monitored in addition to chemical and physical analytes may be beneficial.



# INTEGRATED STRATEGY TO GUIDE MICROBIAL QUALITY MANAGEMENT AT ALPINE KARST WATER RESOURCES: PART II – TOWARDS FECAL HAZARD CHARACTERIZATION AND RISK ASSESSMENT

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**W**ater resources from alpine and other mountainous karst aquifers play an important role for water supply in many countries. World-wide approximately 25% of the population are fed by drinking water resources from karst aquifers. Karstic catchments require a sustainable protection. The increasing impact to such regions and different land use in the watersheds of karst springs are important reasons to establish early warning systems and quality assurance networks in water supplies. Microbial fecal pollution belongs to the most endangering contaminants in alpine karst aquifers. However, until recently, microbial fecal pollution could only be detected by traditional standard approaches based on individual grab sampling and time demanding cultivation procedures in the laboratory. Hardly any information on the pollution dynamics, origin of pollution as well as associated health-risks (in case of exposure) could be given. Due to this lack of knowledge, a joint effort between the disciplines of microbiology and hydrogeology was undertaken to open the “black box” of pollution microbiology by developing new techniques and strategies which guide resource and water quality management at catchments of alpine karst water resources. The final aim of the effort is to provide a sustainable framework which supports decision making at all required time scales of information (e.g. from near-real-time spring water abstraction management, within the resolution of minutes, up to catchment protection practices, within the time frame of months to years). The presentation regarding the microbiological aspects will cover, i) results on the evaluation of standard faecal indicators to indicate human and animal fecal pollution in the considered alpine environment, ii) the establishment of new molecular fecal source tracking technologies to guide target-oriented catchment protection, and finally, iii) to discuss strategies for translating the observed faecal pollution hazards into associated health-risks to assess the required level of water treatment (disinfection) for a sustainable drinking water supply according to health-based quality targets.

# INVESTIGATING AND REMEDIATING CONTAMINATED KARST AQUIFERS

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Subsurface investigations of contaminated karst aquifers are generally regarded as extremely difficult. The difficulty is partly a result of the significant heterogeneity and anisotropy created by the existence of open and plugged ramiform conduit systems, but is also a result of the existence of an overlying epikarst. Even more intractable is the effective remediation of contaminated karst aquifers for basically the same reasons. The difficulties associated with investigating and remediating karst aquifers are further exacerbated when situated in areas with complex folding and faulting of strata. Couple the specifics of various contaminant types of varying degrees of reactivities, densities, and miscibilities (e.g., VOCs, LNAPLs, DNAPLs) with the complexities typical of karst terranes and the limitations of comprehensive karst investigations and effective remediation techniques quickly become evident. Typical remediation techniques, such as pump and treat operations, in situ thermal treatments, in situ chemical oxidation, bioremediation, and monitored natural attenuation all exhibit significantly reduced performances relative to other types of aquifers. Partially in recognition of the challenges associated with specific contaminant types and groundwater investigations and remediation techniques when applied to contaminated karst terranes the U.S. EPA developed the concept of a TI (Technical Impracticability) waiver in which remediation below MCLs (maximum contaminant levels) may not be required. Very few TI waivers have ever been issued, however and obtaining a TI waiver is quite formidable. Remediation down to MCLs is a desirable goal, but the vagaries of karst terranes fully justify the concept of a TI waiver at some complex sites.

**Disclaimer:** The views expressed in this paper are solely those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

# DELINEATION OF A MAJOR KARST SPRING BASIN WITH MULTIPLE INPUT POINTS, ROARING RIVER, TENNESSEE

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The understanding of contaminant transport and the communication between surface water and a karstic aquifer requires a detailed hydrologic investigation, including installing several stage monitoring stations, establishing rating curves, collecting continuous discharge data, and dye tracing. The Boils in Jackson County, Tennessee is one of the largest springs in the state (average discharge  $3 \text{ m}^3\text{sec}^{-1}$ ) and the site of a Wildlife Management Area as well as two State Scenic Rivers. The karst system occurs mostly in the Ordovician Leipers Limestone unit. In the upper basin there are risks for contamination from municipal sewage plants and a proposed landfill. Throughout the basin many residents rely on the aquifer as a drinking water source and for agriculture. A semi-quantitative dye trace was carried out by injecting rhodamine WT at a swallet on Spring Creek, a Tennessee State Scenic River, 9.4 kilometers from the Boils, and injecting Tinopal, an optical brightener, at a swallet on the Roaring River 1.8 kilometers from the Boils. Dye was recovered by collecting water samples, activated carbon, and cotton. The injected RWT traveled to the Boils (a distance of 9.4 km) in approximately 24 hours, implying little attenuation of contaminants. This is the longest dye trace carried out through this geologic unit. A quantitative trace is planned in order to determine the attenuation and travel time more precisely, from different swallets in the basin, to the Boils.

## BASSETT'S CAVE BERMUDA

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In June, 2014, the Government of Bermuda contracted with Southern Environmental Technologies, Inc. to map Bassett's Cave on the island of Bermuda. The cave is located under a former U.S. Naval Air Station Annex and suffered severe environmental impact and degradation during military activities from 1940 until 1990. There is thick viscous oil floating on the tidal pools in the cave and steel drums are visible in one of the entrances. Four cavers from Tennessee, Marty Abercrombie-Environmental Scientist, John Hoffelt-Professional Geologist, JP McLendon- Ecologist and Maureen Handler-Environmental Engineer (the owner of Southern Environmental) travelled to Bermuda to map the cave, flag the cave on the surface, estimate the quantity of oil in the cave and sample the drums. In addition, Southern Environmental worked with the site General Contractor to advise on implementing remediation in the cave. During mapping of the cave, historic signatures dating back to 1779 were discovered. Another discovery is the appearance of unusual effects (biological?) on the formations from the environmental impact.

# MOVING BEYOND CASE STUDIES: RESEARCH EXAMPLES FROM MOUNTAINTOP REMOVAL COAL MINING

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**M**ountaintop removal is an aggressive form of surface coal mining practiced in Central Appalachia. People who live near these mining sites express concerns about the damage to water and air quality caused by this mining, and the corresponding impacts on public health, but until relatively recently empirical evidence was lacking. This presentation will describe the progression of a research line proceeding from secondary analyses of epidemiological data, to community health surveys, to the beginnings of environmental exposure assessment studies in laboratory and community settings. Early studies documented significantly higher covariate-adjusted mortality rates for populations in mining versus non-mining areas. Other secondary analyses revealed higher rates of poor birth outcomes and adult morbidity indicators. Community surveys helped to confirm health disparities on finer geographic scales. Environmental sampling began to document the levels and types of air and water contaminants present in mining communities, and most recently, the first connections have been made between environmental conditions and biological markers of effect. Particulate matter from mining communities, for example, has been shown to promote lung cancer progression in vitro. More remains to be done, but the example of mountaintop removal provides a 'case study' in moving from anecdotal to research evidence on an environmental health concern. Lessons learned may be useful in developing a research base to understand public health impacts from karst groundwater contamination.

# STORMWATER RUNOFF CHARACTERIZATION AND TREATMENT SYSTEM EFFICIENCY ANALYSIS IN MAMMOTH CAVE NATIONAL PARK

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**M**ammoth Cave National Park is home to the world's longest mapped cave system including a distinct karst topography and a biologically diverse cave ecosystem. With more than half a million visitors annually, the cave system is vulnerable to anthropogenic contaminants from human activities carried into the karst system by storm runoff. The objectives of this research were to characterize the major pollutants in storm runoff, and analyze the treatment efficiency of the current filter system with the objective of improving efficiency. Tracer studies were conducted to establish flowpaths for the monitoring network on the surface and in the cave. Regression analysis found correlations between various chemical parameters and parking lot size or storm intensity and frequency. In general, the storm filters were effective at removing hydrocarbons (>90%), but less effective at removing copper (Cu), zinc (Zn) and quaternary ammonia compounds (QAC). Sorption studies using filter materials, zeolite, perlite, and activated carbon, indicated that the filters adsorbed 65% and 52 % for zinc and copper, and 26% for QAC within 24 hours. The lessons learned from this study show that the chemistry of parking lot runoff varies by parking lot size and storm properties, and alternative stormwater management practices should be considered to improve the treatment efficiency.

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## WATER TRACING TESTS AND PUBLIC HEALTH IN KARST AREAS

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**W**ater tracing using injected fluorescent dyes or salts is an established method to study water movement in karst aquifers. The tests determine connections between points where water sinks and reappears in springs and wells. Quantitative monitoring of tracer concentration over time at the resurgences can also help predict the movement of contaminants or pathogens through the aquifers. A test reported from Switzerland in 1872 used NaCl to show that the source of a typhoid epidemic was sewage in a stream sinking in a neighboring valley and the tracer reached the town's water-supply well within 24 hours. The town of Lewisburg, West Virginia is situated on a mature karst plain with no nearby surface streams, and simply allows all the domestic wastewater to disappear into the porous epikarst without any treatment. Tracer tests conducted in the 1970s determined that the sewage reappeared 10 km away at Davis Spring on the Greenbrier River with a travel time of 18 days. The town of Union also lacked sewage treatment and this water reappeared at a spring 2.7 km distant with a travel time of less than 2 days. The family using this spring for their drinking water reported a case of typhoid fever. Union still discharges (treated) water to a sinking stream. Walkersville, Maryland suffered a broken main sewer line that leaked undetected into a sinkhole for three days and a tracer test (and bacteria levels) forced the closure of the town well for several weeks.



# CURRENT STATE OF METAL TOXICITY AND REMEDIATION IN THE TRI-STATE MINING DISTRICT, USA

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The Tri-State Mining District of Kansas, Missouri and Oklahoma (TSMD) experienced roughly a century of mining, ending around 1970. Impacts included: non-ore waste rock disposed near production centers, emissions from smelters (dispersing metals into top soils), and post-mining subsidence associated with abandoned mine shafts. In the early 1980s, the USEPA designated Tar Creek (OK), Cherokee County (KS) and Oronogo-Duenweg (MO) as Superfund sites. Areas within the TSMD still exhibit Cd, Pb, and Zn concentrations exceeding safe levels. Data show that sediment metal median values remain at or above guidelines recommended for aquatic habitats, and the highest Pb and Zn concentrations spatially are associated with the former mining and smelting centers. Increased levels of contaminants within aquatic sediments has been correlated with a decrease in biodiversity, and population sizes of invertebrates, mussels and fishes from stream reaches located downstream of mining activities. Because invertebrates and fish are important food sources, the potential for biomagnification and health impacts is considered high. Accumulation of Pb and other metals is consistent with studies from other regions. Birds studied in the TSMD had increased blood, liver and kidney concentrations of Pb, Cd and Zn compared to birds from reference sites. Zinc was noted to have the greatest impact in waterfowl. These observations imply that mine wastes remain a problem and further remediation is needed. Continued monitoring and remedial practices are needed until affected areas recover completely.

# IMPROVING THE KARST GROUNDWATER CATCHMENT AREA ISOHYET MAP OF RÍO TANAMÁ, ARECIBO PUERTO RICO, USING A GEOGRAPHIC INFORMATION SYSTEM SOFTWARE METHOD

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This investigation focuses on the improvement of the Charco Hondo (CH) isohyetal map method created in the investigation by Martínez, 2014. It is important since there is no catchment area determined for CH by the United States Geological Survey (USGS). The goal is to obtain a faster and more cost-effective method to describe the physical boundaries of a karst groundwater catchment area. By correlating discharge data from the USGS, and rainfall data from the National Oceanic and Atmospheric Administration, Advanced Hydrologic Prediction Service (NOAA, AHPS), the resultant map should show the physical boundaries of the catchment area in CH, at Río Tanamá. High rainfall resolution data obtained from NOAA, AHPS; and different interpolation tools in the Geographic Information System (GIS) program ArcMap 10.1 were used to improve the isohyetal map of Río Tanamá at CH region. As part of the investigation, a yearly record measure of the Total karst Flow (TKF), and a calculation for the drainage area in CH and Near Utuado (NU) was estimated in Excel. However, the resultant map in this investigation does not show a direct relation with the boundaries of the catchment area in the study area; the results proved the relation between discharge graph high peaks and rain events.

# ON THE IMPLEMENTATION OF ENVIRONMENTAL INDICES IN KARST

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**P**eculiarity of the karst environment, related to a number of specific geologic and hydrologic features, makes it a unique setting on Earth, characterized by high fragility and vulnerable to many geo-hazards, and to a variety of anthropogenic disturbances as well, including contamination problems. Even though its uniqueness is well recognized since a long time, only in recent years efforts have been made to develop approaches and methods specifically dedicated to karst environment. The use of approaches dedicated to karst represents a mandatory step in the management of karst terranes. It highlights to stakeholders, land managers and people living in karst, the fragility of such environments, and the need to safeguard them and the natural resources contained therein. First and foremost is the groundwater. In this article we review the main indices proposed in the literature during the last 10 years, and discuss them, taking into account the different scales of application (national, regional, protected karst area, show cave(s), single cave, etc.), their practical implementation, and the related problems and difficulties.

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# ENVIRONMENTAL EXPOSURES AMONG PREGNANT WOMEN IN THE NORTHERN KARST REGION OF PUERTO RICO

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Puerto Rico has elevated rates of preterm birth and other adverse health conditions, as well as the potential for high exposures to environmental chemicals which may contribute to recent adverse health trends. However, limited information exists on current human exposures to environmental chemicals in Puerto Rico. Preliminary findings will be presented from an ongoing cohort study of pregnant women in the Northern Puerto Rico karst region as part of the “Puerto Rico Testsite for Exploring Contamination Threats (PROTECT)” program. Using a biomarker approach, exposure levels to a wide range of potentially hazardous chemicals have been explored, as have some early indicators of biological response. These results are being used to compare exposure distributions with other populations, study pregnancy risks related to exposure, and inform future efforts for intervention.

# THE KARST REGIONS OF PUERTO RICO

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Late Cretaceous and Tertiary carbonates are the cave and karst formers of Puerto Rico. About 98% of Puerto Rico's 2400 km<sup>2</sup> of karst is developed on Oligocene-Pliocene carbonates restricted to the north (90%) and south (9%) coasts, with the remainder on Cretaceous limestones scattered throughout the interior. The climate is humid tropical, with rainfall of about 2 meters per year on the karst, except the rain-shadowed south. Some features, such as *mogotes*, *cockpits*, *ramparts* (huge case-hardened river levees), and *bellholes* formed by bats, appear to have little expression outside the tropics, and are likely to have climate-specific restrictions.

Recent convergent plate compression arched the island, exposing older plutonic and metamorphic rocks in the cordillera, and likely contributed much of the jointing in the carbonate rocks. Cosmogenic dating of surfaces in the Luquillo Mountains of the east indicate this occurred by about 5 My BP. Uplift of the Tertiary carbonates was probably less than 600 m; high points of the northern karst rarely exceed 500 m a.s.l. today. Recent activity on this coast (Atlantic) has uplifted a marine terrace to about 80 m elevation, similar to elevations of nickpoints on some of the northern rivers, and in major caves. The lowered sea levels of the Pleistocene significantly enhanced the relief, and encouraged karst development below current sea level. As a result, the largest spring on the island – Aguas Frias – descends below sea level 15 km inland, and then ascends 30 m before resurging in the bank of the Río Manatí.

The northern rocks mostly dip gently northward 4-5° to the Atlantic, and differential erosion has produced scarps, and/or long chains of mogotes along the E-W strike. Large level areas are covered with remnants of the reddish “blanket sands” (quartz and clays) of likely longshore drift. Rugged expanses of mogotes that drain into cockpits dominate most of the remaining area, although less-soluble beds of the diverse Cibao Formation produce expanses of rolling hills, and some streams that drain to swallets of the Aguada Limestone. Truncated and alluviated dry valleys, and caves, record a long history of stream invasion from the silicic highlands, and eventual capture, chiefly near the southern fringe of the karst. With care, the “chaos” of cockpit karst is often recognizable as relics of progressive dissection via cockpit development within former valley thalwegs that crossed the karst. The few through-flowing karst rivers have entrenched 100-200 m in prominent canyons, and receive outflows from numerous springs in the neighboring holokarst platforms. These rivers also serve as convenient boundaries of the five karst blocs of the north.

For its size, Puerto Rico has a large background of karst literature (dominated by Watson Monroe's work), although much less concerns the 100s of caves except for accounts of exploration. Cave orientations are mostly controlled by the strike and dip, with occasional faulting or major joint sets playing a role. The location of major caves or systems appears related to long-lived dominance of the initial points of invasion on the Lares Limestone, by streams that have integrated either on the volcanic/plutonic highland rocks, or on the Cibao Formation sandwiched within the body of the karst.

Most large caves, then, are found near the southern karst boundary, or in the uppermost units of the Cibao. Following initiation of a major conduit, a series of vertically superposed galleries develop as base levels migrate downward in response to vertical uplift. Recent cosmogenic dating in the famous Rio Camuy System indicates that by at least 4.5 My BP the Camuy had developed a very large conduit that flowed eastward on the strike to join the Rio Tanamá. By 4 My BP it had swiveled 90 degrees north to flow independently in its modern down-dip course.

# CAVE CONDUITS AS RECEPTACLES OF TRASH AND SEPTIC TANK CONTAMINATION OF KARST IN PUERTO RICO

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Currently, over 40 major trash accumulation sites are known within caves of Puerto Rico, or in streamways leading to them. In addition, the routine use of septic tanks above and within caves and dolines in the North Karst is probably an even larger health problem.

The common types of trash are typical of households: e.g. washing machines, refrigerators, stoves, used tires, mattress beds, etc. Mobility in these trash sites can be initially categorized as stream caves vs. dry caves. Trash dumped in streams travels long distances above and below ground as the discarded material is gradually pulverized and transported by conduit-filling floods. The Camuy Cave System is a classic example of a fully-formed river carrying material from upstream surface dumps into and through several kilometers of large conduits to its resurgence. Dry dump caves tend to be vertical pits (some exceed 50 m deep) at the bottom of which the trash accumulates, but which stays in situ.

Septic tanks in the North Karst number in the tens of thousands, often constructed with complete disregard of EPA regulations and common sense. The classic example is that of the Montserrate urbanization 20 miles west of San Juan. This area of hundreds of residents contained at least 37 known collapse sinkholes prior to construction, most of which lead to caves 5-10 m below ground, and of which many connect beneath homes and buildings. Surface septic tanks discharge directly into the caves, the majority of whose entrances are also filled with voluminous trash.

# USING ENTERIC PATHOGENS TO ASSESS SOURCES OF FECAL CONTAMINATION IN THE SILURIAN DOLOMITE AQUIFER: PRELIMINARY RESULTS

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The Silurian aquifer is an important, but vulnerable, source of drinking water in northeastern Wisconsin. In areas where soils are thin, there is a history of “brown water” events that occur in response to groundwater recharge. Sampling programs in Kewaunee County indicate that ~42% of wells in the Town of Lincoln do not meet drinking-water standards due to the presence of bacteria and/or exceedance of the US EPA nitrate standard. As resource managers try to address these water-quality problems, there is no consensus as to whether the main source of fecal contamination is human or bovine waste. Dairy farming and associated crop production comprise the primary land use and manure is commonly applied to crop land. Within the town, there are approximately 13,500 cattle and 334 households.

We completed a pilot project to assess whether sampling wells for enteric pathogens could be an effective method of assessing sources of fecal contamination. Sampling was conducted in May 2014 and involved pumping ~800 L of groundwater through hemodialysis filters. Quantitative polymerase chain reaction (qPCR) methods were used to determine genome concentrations for microbial targets divided into three fecal-source groups: 1) human-specific microbes; 2) bovine-specific microbes; and 3) non-specific microbes found in fecal wastes of humans, bovines, and other animals. Results indicate that 7 of the 10 sampled wells were positive for fecal contamination. Future efforts will 1) use quarterly samples to distinguish septic versus bovine sources of contamination and 2) determine the timing of peak transport for viruses and indicator bacteria.

# FATE, TRANSPORT, AND EXPOSURE OF EMERGING AND LEGACY CONTAMINANTS IN KARST SYSTEMS: STATE OF KNOWLEDGE AND UNCERTAINTY

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It is well known that the same characteristics that make karst groundwater systems highly productive also make them very vulnerable to contamination. Once in the subsurface, many contaminants move along and spread across flow lines, interact with media and environmental compartments, and react with chemical and biological entities. All of these processes occur within a highly dynamic and heterogeneous framework that affects the mobility, persistence, and potential exposure of humans and wildlife. Fundamental knowledge exists on many of these processes and several predictive and characterization models have been developed and applied to karst systems. Yet tremendous challenges and uncertainty are faced when trying to predict exposure, implement remedial actions, and manage contaminated systems, particularly in a changing world. This paper discusses the state of knowledge, modeling capabilities, and sources of uncertainty when assessing the fate, transport, and exposure of legacy and emerging contaminants in karst systems. Although applicable to many sites, the discussion will be framed around particular examples of extensive contamination in the karst region of northern Puerto Rico, and how these compare to more densely lithified karst systems associated with continental karst. It will focus on contaminants related to industrial, agricultural, and personal care activities. Despite the advancements made on understanding and modeling fate and transport processes, large uncertainty remains on: source and system characteristics, scale-dependent model applicability, spatiotemporal data resolution, and the effect of hydrologic conditions and anthropogenic intervention.



# FACTORS INFLUENCING THE OCCURRENCE AND THE FATE OF *E. COLI* POPULATIONS IN KARST HYDROSYSTEMS

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**A**ssessment of the microbial quality in the water environment, including the spread of antibiotic-resistant fecal bacteria and their corresponding genes, will be one of the major challenges of the next decades. Among aquatic environments, karst aquifers represent one of the most important freshwater resources supplying water of 25% of the global population and 33% of the French population.

We recently conducted multidisciplinary studies - associating hydrogeologists with clinical and environmental microbiologists in order to determine the vulnerability to contamination by the fecal bacterial indicator - *Escherichia coli* (*E. coli*) - including anti-bioresistant strains.

We focused this study on a small karst system developed in chalk in Upper Normandy. This system has been extensively monitored for water, particle, and solute transport during the past 15 years, and belongs to the French national observatory network on karst (INSU/CNRS). It is a small binary system (~12.5 km<sup>2</sup>) which comprises a surficial watershed on the chalk plateau drained by a permanent creek (the Bébec creek). The creek is engulfed into a sinkhole connected to the karstic spring located at the foot of the plateau. Finally, a well used for water supply is located 130 m downstream of the spring.

Abundance of viable or culturable *E. coli* was monitored on the surficial watershed (i.e. the upstream part of the system) and at the spring downstream under contrasting hydrological conditions (dry and wet). Both the resistance of the *Escherichia coli* population (436 isolates) to 17 antibiotics and the ability to survive in oligotrophic conditions at 10 °C were investigated. In addition, the occurrence of *E. coli* in biofilms at the outlet of the system was analysed by *in situ* experiment.

The abundance of culturable *E. coli* in the karst aquifer reflected the previous contamination of the creek by run-off and soil leaching, both depending on the hydrological conditions and the land use. The contamination of the water by culturable *E. coli* decreased by about one to three orders of magnitude from the sinkhole to the well, mainly due to the strong dilution of the surface water within the groundwater. However, we demonstrated that *E. coli* could be trapped in biofilms.

Viable *E. coli* were detected along the flowpath (upstream to downstream: sinkhole-spring-well) even during the dry period, whereas culturable *E. coli* were not detectable in the water. After a rainfall event, increasing contamination is combined with an input of a population of culturable *E. coli* able to persist in water less than two days and mainly resistant to antibiotics. Analysis of the phenotypic antibiotic resistance show that 10 - 23% of these isolates are resistant to two or three antibiotics. At the sinkhole, the structure of *E. coli* population in water -i.e. the ratio of A to B1 phylo-groups- varied with the hydrological conditions and a sub-population of more persistent *E. coli* strains are circulating in water in the dry period. Indeed, irrespective of the hydrological conditions, the karst system may also act as a permanent reservoir of viable *E. coli* even when culturable *E. coli* became undetectable in the drinking water pumped out at the well during dry period.

In 2015, the main conclusions obtained in karst aquifer and rivers were reported to the stakeholders and to the French Ministry of Health, to assess the microbiological risk due to the spread of antibiotic resistant bacteria, according to the DPSIR (Driving forces- Pressure- State- Impact- Response) concept.

# DEVELOPMENT OF THE ELECTROCHEMICAL TECHNOLOGIES FOR REMEDIATION OF CONTAMINATED GROUNDWATER

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**K**arst aquifers are highly productive but extremely vulnerable to contamination. Since groundwater transport occurs under relatively high flow rates in aquifers in karst terrain, the contamination spreads unfiltered to wells and other drinking water sources connected to the aquifer. Therefore, development of efficient technologies to remediate contaminated groundwater and minimize health risks is challenging but necessary. Electrochemical based technologies are a viable option for treatment of groundwater in karst regions. Our team is evaluating the use of solar panels to generate a low-level direct current through electrodes in wells and enable manipulation of groundwater chemistry by *in situ* electrolysis leading to reduction and/or oxidation of contaminants. This approach has several advantages: 1) it is sustainable and driven by a renewable energy source, 2) it is environmentally friendly because it does not require the addition of solutions or chemicals into groundwater, and 3) the rates of redox reactions can be easily controlled by adjusting electric current intensity. Currently, we are optimizing the performance of the electrochemical reactors to induce reduction and/or oxidation transformation mechanisms of contaminants. The reactors are designed to be implemented in the wells and operate under groundwater circulation; they are tested for different electrode properties such as materials, dimensions, arrangements and modes of operation as well as groundwater conditions such as flow and content of naturally occurring substances. The laboratory setups tested showed removal efficiency of more than 99% for trichloroethylene, which is primary contaminant of concern in our study. Solar driven electrolysis will be implemented in wells for *in situ* degradation of contaminants through sustainable and easily controlled formation of reactive species.

# WHERE IS THE GREATEST POTENTIAL FOR SUPERFICIAL CONTAMINATION IN THE NORTH COAST LIMESTONE AQUIFER OF PUERTO RICO?

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The two most important aquifers in Puerto Rico are the North Coast limestone karst and the alluvial South Coastal Plain. Because of its karst nature, traditionally the North Coast limestone aquifer is classified as uniformly being at high risk. There are a number of unused types of data that can be used to look at the question if the North Coast limestone can be classified as uniformly at risk or whether it should be subdivided into smaller management units. Compared to recharge water, old aquifer water is warmer, has higher dissolved solids, and lower oxygen, suspended solids, nutrients, and aerobic microbes. The correlation between hourly groundwater levels and water temperature in observation wells was used to identify two areas at higher risk from superficial contaminants. The two areas are the adjoining municipios of Quebradillas/Camuy and Manatí/Vega Baja. The US Geological Survey has on the Internet real-time groundwater level and rainfall data from only one station in the North Coast limestone aquifer, Florida 7. This observation well is extremely well connected to the surface. Between 22 May 2015 and 18 September 2015 this station had 28 recharge events. This observation well has measureable increases in water level with only 5 mm of rain. On average this station reaches a maximum water level 2 hours and 40 minutes after a rain event. In the future it should be possible to directly measure the travel time from rainfall to production water by measuring the temperature of rain and production water at producing wells.

# KARST- FITTING REGULATORY SQUARE PEGS INTO ROUND HOLES

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Regulation of karst to protect groundwater and public health poses unique challenges to regulators. First and foremost, often no regulatory authority is assigned responsibility for karst. For example, in the United States the federal government lacks authority to directly regulate karst. State governments hold authority to regulate, but often fail to do so. Therefore, regulation of karst in the United States mostly falls to local governments, who often lack the resources and expertise to effectively regulate karst.

In addition, the regulation is required (often constitutionally) to apply uniformly to the regulated community to avoid claims of arbitrary and discriminatory treatment. Uniform regulation has been crafted in most settings. However, the karst environment is chaotic and each situation presents unique circumstances that call for variable approaches. In this context, standard regulatory approaches often fail to protect public health, and creative approaches often face legal challenge.

This presentation describes the regulatory dilemma surrounding karst regulation and analyzes various regulatory approaches to karst. In addition, the speaker considers a variety of non-regulatory approaches that, in conjunction with regulatory approaches, may more effectively protect public health. The presenter concludes that education- of regulators, government officials, and citizens- must precede any regulatory or non-regulatory measures if those measures are to effectively protect public health and karst resources.

# SPATIOTEMPORAL ASSESSMENT OF CVOC CONTAMINATION IN KARST GROUNDWATER SOURCES AND EXPOSURE AT TAP WATER POINT OF USE

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Well-developed conduit porosity and highly transmissive zones characterize karst terrains. These characteristics not only make karst aquifers highly productive and important freshwater resources for human consumption and ecological integrity, but also impart high vulnerability for contamination. As a result, karst groundwater systems may serve as a significant route for contaminant exposure and lead to potential public health impacts. Chlorinated volatile organic contaminants (CVOCs) are of particular concern because of their ubiquitous presence in the environment and potential health impacts. The study assesses potential associations between contamination of karst groundwater and that at the tap water point of use. GIS technology and statistical methods are applied to perform spatiotemporal analysis of the collected data. The analysis incorporates data gathered from regulatory agencies and current groundwater and tap water samples collected from residential homes. Results show extensive presence of CVOC in groundwater and tap water. Several CVOCs, including carbon tetrachloride, tetrachloroethene, and trichloroethene are found at higher frequencies and concentrations in groundwater than tap water. Chloroform is found at higher frequencies and concentrations in tap water than groundwater. Spatially, contamination is found throughout the study area, with some hot spot clusters in certain regions. Temporal analysis shows a decreasing concentration trend for CVOC in groundwater, and high variability with no marked trend in tap water. Spatiotemporal analysis suggests that contamination comes from multiple sources and that association between tap water and groundwater contamination depends on the type of contaminant, spatial location, and time.



# BEYOND CASE REPORTS: PLACING KARST IN CONTEXT IN PUBLIC HEALTH RESPONSE TO GROUNDWATER CONTAMINATION

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There are several reports of elevated levels of lithium in drinking water associated with effects on mental health outcomes and violent crime rates. Lithium has been found in levels therapeutic for psychoactive efficacy up to levels high enough to cause mild toxicity. These findings occurred in or near areas with underlying karst aquifers in the United States, Europe, and South America. The drinking water sources for the affected areas included both groundwater and surface water. The nature of the groundwater flow system and its direct connection to the surface in karst areas suggests that drinking water sources may be affected by karst processes. These studies are reviewed along with selected reports of other drinking water contaminants found in similar karst areas. Waterborne illness is often specific to drinking water supply, associated with storm events, or is accompanied by breach of infrastructure into geologic structures. These factors in the presence of karst features may result in wider, more unpredictable spread of illness and might not otherwise be amenable to usual engineering solutions. A conceptual approach is proposed for public health practitioners to evaluate disease and health epidemiology as a function of geologic causes of drinking water issues and to consider karst effects as a particular category or subset of medical geology.

**Disclaimer:** The views expressed in this abstract are those of the author and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

# HYDROLOGIC ANALYSIS OF A POPLAR-BASED PHYTOREMEDIATION SYSTEM

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An evaluation of the hydrologic performance of a poplar-based system for containing impacted groundwater was conducted over a five-year period at the Ischua Creek Habitat site in Machias, NY. An important parameter needed for the engineering design of poplar-based systems is the rate of groundwater uptake by the trees (evapotranspiration of groundwater =  $ET_G$ ). Using field data from monitoring wells at the site, the method of White (1932) was applied to estimate the  $ET_G$  on a continuous daily basis. The White method estimates water consumed by trees based on diurnal fluctuations in groundwater elevations observed in well hydrographs. To perform the extensive five-year data analysis, an algorithm for automating the White method calculations was developed and refined. The statistical analysis of the results showed that the highest median  $ET_G$  values occurred in the third year of poplar growth (2014) for all the wells. Furthermore, the analysis demonstrated that for some years the wells with the highest median  $ET_G$  values were located distant (more than 15 meters away from the phytobarrier), in contrast to expected behavior. In general, robust relationships between  $ET_G$ , poplar growth and proximity to the phytobarrier could not be established for the period of study. Therefore, it appears the White method may not be an appropriate technique for evaluating the performance of a phytobarrier. Possible reasons include the lack of complete areal coverage by the phytobarrier, the young age of the trees, data scatter in the observed hydrographs, and a variety of simplifying assumptions associated with the method.

# QUANTIFICATION OF WASTEWATER INFILTRATION AND TRANSPORT PROCESSES IN KARST AQUIFERS

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**K**arst groundwater resources are highly vulnerable with respect to anthropogenic impacts, such as wastewater infiltration, because of focussed recharge and the rapid transport of dissolved substances in highly permeable conduit systems. Here, examples are presented of approaches in the quantification of wastewater impact on potable groundwater, which poses problems in many parts of the world as well as the transport of wastewater borne components in the phreatic zone of a karst aquifer.

For the quantification of the total flux of wastewater in groundwater discharge, long-term records of chloride concentration of karst groundwater discharge in springs of the Jericho (West-Bank) area were analysed with respect to the wastewater borne component. Chloride is used as an environmental tracer for (1) groundwater recharge estimation and (2) anthropogenic impact quantification. The investigations required the determination of the natural background concentration of chloride in groundwater. It was estimated by a combined use of historical data and a trend analysis for larger springs in the area and a range between 20 and 40 mg L<sup>-1</sup> was found. Together with chloride concentration data for local precipitation, the long-term mean natural groundwater recharge was calculated with the chloride mass balance method. Recharge ranges between 25 and 50 % of the precipitation. The proportion of wastewater-borne spring flow was quantified by a chloride end member mixing model. The springs exhibited a wastewater-borne flow fraction of between 0 and 22 percent, calculated from recent samples.

Mass transport and attenuation processes of trace organics in a karst conduit system were quantified by a multitracer experiment investigating differential transport of selected relevant micropollutants. The conservative tracer Uranine, and the trace organics acesulfame and carbamazepine were injected into a sinkhole as reference tracers together with the reactive compounds atenolol, caffeine, cyclamate, ibuprofen and paracetamol (also known as acetaminophen). The breakthrough of the tracers was monitored at a karst spring at a distance of ca. 3 km. The breakthrough curves of the reactive compounds were interpreted relative to the reference substances. No significant retardation was found for any of the investigated micropollutants. The determined half-lives of the reactive compounds range from 38 to 1400 h (i.e. persistent within the investigation period) in the following order (from high to no observed attenuation): paracetamol > atenolol ≈ ibuprofen > caffeine >> cyclamate. The attenuation rates are generally in agreement with studies from other environmental compartments. The occurrence of the biotransformation product atenolol acid served as evidence for in situ biodegradation within the aquifer system. Finally, a selection of modelling approaches is shown believed to assist in the prediction of transport in matrix-conduit karst systems.

# ADDRESSING HAZARDOUS MATERIALS RELEASES IN KARST TERRAINS

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**K**arst aquifers are one of the most vulnerable aquifer types to contamination from anthropogenic sources. In comparison to other aquifer types, karst aquifers are noted for their high secondary permeability and rapid recharge, groundwater velocities measured in kilometers per day, and little attenuation of contaminants. The release of hazardous materials into a karst terrain can result in a direct and rapid impact to groundwater resources and ultimately, to springs and rivers. Many communities have well developed hazardous materials response (HAZMAT) programs to contain and mitigate environmental hazards. However, first responders as well as resource managers may not understand some of the unique aspects of karst. This can result in unforeseen and potentially catastrophic consequences to public health through contamination of groundwater resources. Releases of fuel have even resulted in even explosive vapors in buildings and sewers.

This presentation identifies common sources of hazardous materials and recommendations for an overall hazardous materials release strategy. This includes preplanning and training with HAZMAT team professionals, identification of potential receptors, source water protection planning, and hazardous materials response strategies in karst.

# RELATIONSHIP BETWEEN ORGANIC MICROPOLLUTANTS AND HYDRO-SEDIMENTARY PROCESSES AT A KARST SPRING IN SOUTH-WEST GERMANY

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In the past a number of parameters (such as turbidity, dissolved organic carbon concentration, particle size distribution) have been proposed as proxies that can be used to detect changes in water quality or contamination at karst springs. However, most of these are not very specific concerning the source of contamination. Organic micropollutants (OMPs) such as artificial sweeteners or herbicides are possible source-specific indicators that can be used in karst catchment areas. Online measurement of electrical conductivity (EC) and turbidity allows for identifying hydro-sedimentary processes by analyzing hysteresis-plots. We have investigated the possibility of combining the OMPs as source specific indicators with online measurements of electrical conductivity (EC) and turbidity. Our investigations were carried out at the Gallusquelle karst spring in south-west Germany during a flood event. Results of OMPs are generally consistent. The legacy compound atrazine (herbicide), which derives from the aquifer matrix, was detectable in the spring water until re-suspended particles appeared at the spring. The herbicide metazachlor, which is present in recharge from cropland, was found to be associated with periods of direct transfer of particles originating from the land surface. The artificial sweetener cyclamate was used as a wastewater indicator, but neither hysteresis plots of EC and turbidity nor any other online parameters were able to indicate the presence of cyclamate following a wastewater spill. Since EC and turbidity are easily measurable parameters, systematic knowledge of relationships of EC turbidity hysteresis-behavior to OMPs might assist in the sustainable management of raw water within karst catchments.



# MICROBIAL CONTAMINATION IN KARST: FROM MONITORING TO PROCESS COMPREHENSION

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**M**icrobial contamination remains by far the most common cause of quality degradation in karst groundwater resources and – in terms of drinking water supply – is highly relevant from a public health perspective. Significant here is the occurrence of fecal microorganisms at karst springs as well as its prediction on the basis of reliable hypotheses regarding specific transport and attenuation processes.

Monitoring which is well-adapted and which extends beyond conventional fecal indicator bacteria analyses – i.e. the detection of pathogenic bacteria and enteric viruses, or the application of human and ruminant molecular-dependent microbial markers – provides greater insight into the origin and fate of fecal contamination. Such impact information can be integrated into the framework of a general behavior scheme for microorganisms in karst settings. The total cell count represents another innovative parameter for microbial characterization of groundwater in this context.

The simultaneous interpretation of diverse microbiological parameters represents a promising tool for source and pathway tracking – including storage and mobilization issues – and is particularly conclusive when viewed in relation to other markers, such as solute micropollutants. More quantitative information on transport behavior can be obtained from tracing experiments employing specific microorganism types or appropriate particulate surrogates. In this way, diverse processes can be identified and distinguished, such as preferential migration due to exclusion phenomena, interaction with differing surfaces encountered in the subsurface and associated attenuation, inactivation during storage or particle-attached transport.

Monitoring data in conjunction with in-situ techniques provide the basis for process comprehension and allows the establishment of enhanced conceptual and transport models in relation to microbial contamination and karst systems in general.

# RECHARGE AND WATER-QUALITY CONTROLS FOR A KARST AQUIFER IN CENTRAL TEXAS

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The Edwards Aquifer is a prolific karst aquifer system in central Texas that provides drinking water to about 2 million people. The presence of nonpoint source pollution in storm water flowing in Onion Creek can have a direct impact on water quality in the Barton Springs segment of the Edwards Aquifer. To address this concern, the Barton Springs/Edwards Aquifer Conservation District constructed a concrete vault over the entrance to Antioch Cave in the bed of Onion Creek in 1997. This structure was designed to prevent entry into the cave of contaminated storm water by closure of two valves on the vault during storm events. In 2009, an automated system was installed to improve the efficiency of the system by closing the valves at the beginning of a storm pulse and opening the valves when the turbidity of the storm water drops below a certain threshold. Results of water-quality sampling at Antioch indicate that the system is capable of significant reduction of nonpoint source pollution entering the aquifer through Antioch Cave. Over a period in 2010 that included five storm events, approximately 2,436 lbs of nitrogen from nitrate/nitrite, 295 lbs of total phosphorus, and 190,480 lbs of sediment were prevented from entering Antioch Cave. Dye-trace studies have shown that water entering Antioch Cave can reach Barton Springs in about 5 to 7 days. A set of monitor wells near Antioch Cave are used to monitor the potential for movement of contaminants in the aquifer.

# INTEGRATED STRATEGY TO GUIDE MICROBIAL QUALITY MANAGEMENT AT ALPINE KARST WATER RESOURCES: PART I – HYDROGEOLOGICAL INVESTIGATIONS TO ELUCIDATE FECAL POLLUTION DYNAMICS

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**W**ater resources from alpine and other mountainous karst aquifers play an important role for water supply in many countries. World-wide approximately 25% of the population are supplied by drinking water resources from karst aquifers. Karstic catchments require a sustainable protection. The increasing impact to such regions and different land use in the watersheds of karst springs are important reasons to establish early warning systems and quality assurance networks in water supplies. Microbial fecal pollution belongs to the most endangering contaminants in alpine karst aquifers. However, until recently, microbial fecal pollution could only be detected by traditional standard approaches based on individual grab sampling and time demanding cultivation procedures in the laboratory. Hardly any information on the pollution dynamics, origin of pollution as well as associated health-risks (in case of exposure) could be given. Due to this lack of knowledge, a joint effort between the disciplines of microbiology and hydrogeology was undertaken to open the “black box” of pollution microbiology by developing new techniques and strategies which guide resource and water quality management at catchments of alpine karst water resources. In-situ measurements have to be adapted to the local contamination scenario and online and near real-time availability of data are obligatory. As faecal pollution cannot be detected directly in near-real-time, proxy parameters are necessary to be established for on-line monitoring. The targets of the study were (1) to investigate the dynamic of microbial faecal pollution indicators, chemical parameters and environmental isotopes at a high resolution time scale during hydrological events, and, (2) to evaluate the Spectral Absorption Coefficient at 254 nm (SAC<sub>254</sub>) as a real-time pollution proxy for optimised spring water abstraction management. These investigations lay the foundation for advanced microbiological analysis and hazard and risk assessment (see abstract part II), the basis for catchment protection based on the Dominant Process Concept (DPC) - elaborated by the combination of process-orientated hydrogeological mapping and hydrological modelling – and a state-of-the-art multi barrier protection system of drinking water resources.

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# TENNESSEE CAVE LIFE RELATIONAL GEODATABASE

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Cave biology is a growing interest among scientists and conservationists in Tennessee. Better knowledge of subterranean life will assist in classification of threatened and endangered species, assist in conservation prioritization and strategies, and will grow the scientific body of knowledge.

Currently, only a small handful of individuals are actively looking for life forms in caves, most of which are PhDs, a few state and federal employees, and even fewer general recreational cavers. The data being collected by these individuals is often going to very different places. The purpose of the Cave Biology Geodatabase was to bring together as many of these datasets as possible and attempt to standardize and georeference as much of the available data as possible.

# ANTHROPOGENIC NUTRIENT LOADING ON AN EPIGENIC KARST AQUIFER IN SOUTHEASTERN KENTUCKY

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The proliferation of Confined Animal Feeding Operations (CAFOs) around karst is controversial. Although studies have assessed the contamination risk of CAFOs in karst aquifers, little data have been published. This study looks at the loading of nutrients from weekly samples collected May through August 2015 at Grayson-Gunnar Cave (GGC), an 11-km-long cave system in Southeastern Kentucky. Surveyed passages in GGC include two branches of an underground stream with strong connections to surface input—epigenic karst aquifer. The south branch of this watershed includes low-density grazing and residential septic tanks. The north branch includes a poultry CAFO.

Weekly water samples were collected at the cave spring; three samples were also collected from each of the two branches. Analysis of  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ , and  $\text{PO}_4$  were conducted on these discrete samples using a DR2800 spectrophotometer. Contemporaneous data from the cave stream were collected every 10 minutes using a YSI EXO2 sonde.

From the discrete samples, nutrient flux and sources were computed using a mixing model. From the sonde data, we elucidate aquifer behavior during storm events by looking at key indicators of meteoric water input from sinking streams (conductivity, turbidity, and DOM) and conducting correlation analyses to assess 'lag' times between input and output. Preliminary data from discrete samples reveal  $\text{PO}_4$  and  $\text{NO}_2+\text{NO}_3$  levels consistently above the EPA standards of 0.1 mg/L and 1.0 mg/L, respectively. The sonde data reveal twin peaks in water chemistry consistently occurring following precipitation events, likely the result of merging flowpaths from two sub-watersheds.



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# ASSESSMENT OF FLOW AND TRANSPORT PROPERTIES IN AN INTERMEDIATE KARSTIFIED LAB-SCALE PHYSICAL MODEL USING HYDRAULIC AND TRACER RESPONSE ANALYSIS

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**K**arst provides high capacity to transport and storage of large amounts of water. These features make karst vulnerable to potential contamination of hazardous chemical substances. Detecting dangerous pollutants has posed a tremendous challenge, and has increased the interest to delineate and predict flow and transport processes in karst groundwater systems. Characterization and quantification of these processes at the field-scale is limited by low resolution of spatiotemporal data. Processes at the lab scale may not be representative of conditions at the field-scale, but can provide fundamental knowledge on characterization and quantification tools that can be applied at the field scale to enhance resolution. This work presents the development of an intermediate karstified lab-scale physical model (IKLPM) to study fate and transport process and assess viable tools to characterize heterogeneities in karst systems. Flow experiments are conducted to develop tomographic views of hydraulic responses. Tracer experiments are conducted to generate space-dependent temporal concentration distributions (TCDs) that are analyzed to characterize and quantify the variability of fate and transport parameters. Tomographic views and TCDs results show high spatial variability associated with paths of preferential flows. The outcome of this study will lead to characterize preferential flow path zones of potential pollutants such as PCE and TCE in karst groundwater systems that affect human health and the environment. The development of these technologies to predict fate and transport of contaminants will contribute to mitigate its exposure to the communities and reduce public health impact.

# POTENTIAL EXPOSURE OF EMERGING CONTAMINANTS IN KARST GROUNDWATER THROUGH TAPWATER SOURCES

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**K**arst aquifers are extremely productive groundwater systems, providing 20-25% of the global population water needs. They are also highly vulnerable to contamination. Emerging contaminants, including phthalates, are of particular concern because they can easily enter karst groundwater through a wide range of distributed sources and move toward areas of potential exposure to human and wildlife. Many of these contaminants are known endocrine disruptors and potential precursors of adverse reproductive outcomes. Previous studies in the karst region of northern Puerto Rico have shown significant presence of phthalates in groundwater and tap water. This work develops spatio-temporal distribution of phthalates contaminants in groundwater and tap water in this region, and assesses potential correlations between hydrogeological and anthropogenic factors and phthalate contamination. Geographic Information Systems technologies and statistical models are applied to attain these objectives. Results show extensive phthalates contamination in tap water and groundwater samples that vary in space and time. They are detected as mixtures components in areas of high urban and industrial development. Statistical models show that the presence of phthalates in groundwater is significantly related to sinkholes density, hydraulic conductivity of the aquifers and time. Although groundwater serves as route of contamination to tapwater sources, higher detection of phthalates in tapwater (53%) than groundwater (7%) indicates additional sources of contamination in the water distribution system that may be related to land use. The analysis indicates that phthalates persist for long periods of time in karst systems and that hydrogeological factors contribute significantly to their presences in these systems.

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# PUERTO RICO'S KARST PROTECTION –BEYOND THE LAW AND REGULATIONS

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**T**he karst represents 28% of Puerto Rico and it is a vital natural area for its many resources, i.e. biodiversity, spectacular vistas and subterranean rivers and caves. It contains the most productive aquifers of Puerto Rico on which about 500,000 people depend, as well as industry, commerce and agriculture.

After experiencing almost total deforestation by the middle of the last century, the karst region recovered and became the island's heaviest forest cover, with immense value for tourism and other economic activities compatible with its natural values. Yet, by the 1990s we noticed a trend of urban sprawl and infrastructure development in the karst, which imitated what, was happening in other parts of the island where the environment was not as vulnerable as in the karst region. These developments threatened the natural values of the karst.

Thus, we undertook an effort to protect the karst that involved research, public education, and citizen's actions. One of those actions was developing legislation to protect the karst. The effort was successful and Law 292 was enacted in 1999, but the government was slow in its duty to implement the protective measures. Because of this, we were forced to increase our efforts through judicial action against the agencies responsible for the implementation of the law. After considerable years of litigation, a plan and regulations to protect the karst was finalized in 2014 and we are helping the government in its implementation.

# COMPARATIVE STUDY OF SPECIFIC GROUNDWATER VULNERABILITY OF A KARST AQUIFER IN CENTRAL FLORIDA

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The Floridan aquifer system (FAS) supplies water to more than 20 million people in the south east of the USA. As a karst aquifer, it provides resource managers with unique challenges in controlling groundwater contamination due to the direct connections between the aquifer and the surface. In this study a new Geographic Information Systems (GIS) -based index, the Karst Aquifer Vulnerability Index (KAVI), incorporates geologic layers used in intrinsic groundwater vulnerability models (GVMs) plus an epikarst layer specific to karst, with land use coverages to create a specific groundwater vulnerability model. The KAVI model was compared to another specific vulnerability model, the Susceptibility Index (SI). Tabulation of the percentage areas of vulnerability classes reveals the SI overestimates vulnerability for the study area compared to KAVI. Validation of these two models found that KAVI vulnerability levels best reproduced spatially varying concentrations of nitrate in the aquifer. Both sensitivity analysis and the application of a variation index to KAVI confirmed the importance of closed depressions but also aquifer hydraulic conductivity. The inclusion of land use was justified; however, effective weight analysis determined its assigned weight was too high as used in the initial calculation of KAVI.

# DEVELOPMENT AND TESTING OF HYDROGEL BEADS AS POTENTIAL TRACERS OF CONTAMINANT MOVEMENT IN KARST AQUIFERS

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Recent tests conducted with simultaneously released mixtures of tracers have illustrated that solutes alone do not fully represent the range of contaminant fate and transport mechanisms in karst aquifers. Given these studies, and our limited knowledge about contaminant movement in karst settings, it is critical that the toolbox of available tracers be enlarged. Toward this end, we have completed preliminary development and testing of hydrogel bead tracers as proxies for the movement of non-aqueous phase liquids (NAPL). The beads are inexpensive to make, biodegradable, and easily modified. The beads are primarily water (>95%) held in a calcium alginate gel. Modifications of the beads have included (1) adjustments to specific gravity by adding mineral particles or microscopic glass bubbles, and (2) incorporation of fluorescent pigments to aid in bead detection.

The focus has been on the movement and detection of floating beads as proxies for light NAPL (LNAPL). In early tests the beads were collected manually; later the bead movement was quantified by exciting the fluorescence in the beads with LED lights and video-recording the movement. The video was then processed to separate the colors, calculate the pixel intensity of each frame, and plot the intensities through time to generate break-through curves.

In field demonstrations, the beads traveled faster than the accompanying solute during higher discharge (140 L/s) and slower than the solute during lower discharge (9 L/s). Overall the field tests confirmed the need for more studies and tools to better understand NAPL transport.



# CAVE MONITORING RESULTS FROM CUEVA LARGA, PUERTO RICO

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A cave monitoring study has been going on since 2012 at Cueva Larga in Puerto Rico to elucidate the complex epikarst-cave-atmosphere processes influencing speleothem growth and climate proxy variations recorded in cave sediments (speleothems). Cave monitoring studies are essential to interpret speleothem climate records correctly. A suite of environmental cave atmosphere variables (cave air pCO<sub>2</sub>, temperature and relative humidity), carbonate precipitation experiments and outside weather station observations were collected at near monthly or higher resolution.

The results show that carbonate precipitation in this tropical cave primarily occurs during winter months when increased cave ventilation boosts carbonate oversaturation of the drip water. This might cause a seasonal bias towards the winter growth season in speleothems from Cueva Larga. Drip water samples were analyzed for their isotopic and trace element composition. They lack short term or seasonal variability indicating dominant diffuse seepage flow and a well-mixed epikarst reservoir above the cave. This indicates that the cave is probably well suited for paleoclimate studies especially focusing on multi-decadal climate variations.

## CONTAMINANT TRANSPORT IN KARST AQUIFERS: SYSTEMATICS AND MECHANISMS?

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**K**arst aquifers differ from aquifers in porous media by the highly diverse pathways by which water and any associated contaminants travel from recharge to discharge. The effective hydraulic conductivities may vary by 10-12 orders of magnitude between alternate pathways through the same aquifer. There are three distinct contributions to the permeability: a system of pipe-like conduits with varying degrees of development and integration, a system of solutionally-modified fractures, and the primary permeability of the rock matrix. For any given aquifer, hydraulics and response to contamination inputs depend on the sources of recharge, the specific mix of permeability components, and the physical properties of the contaminants – in effect a matrix of interactions.

Categories of contaminants include water-soluble compounds, both organic and inorganic, low solubility liquids both heavier and lighter than water, and particulates, organic and inorganic, ranging in size from nanometers to meters. Inputs are through sinking streams, storm flow into closed depressions, and infiltration through soils that may be thin and discontinuous. Natural discharge is typically through large springs that are frequently used as water supplies. Features that separate karst aquifers from porous media aquifers are large aperture pathways that permit particulate contaminants to enter the aquifer with little filtration, localization of flow paths into conduit systems which constrict contaminant concentrations to a narrow pathway instead of spreading into a plume, high velocity flows which can move particulates and also transmit contaminants rapidly from point of injection to point of discharge.

Storm flows are exceptionally important in the transmission of contaminants. Storm inputs raise the hydraulic head in the conduit system, increase both flow volume and velocity, and can flush both clastic sediments and contaminants that have remained in storage in the conduit system. During base flow, the conduit systems act as drains with hydraulic gradient in the surrounding fracture and matrix pointing to the conduit. During storm flow, increased head in the conduit reverses gradients, forcing contaminated storm water back into the fractures where it may intercept wells. Rising water levels can force the fumes of volatile organics upward to reach sinkholes and basements. Flooded surface streams may reverse the gradients in the master conduit systems and force contaminated surface water deep into the aquifer.

# SELECTED MICROPOLLUTANTS AS INDICATORS IN A KARST CATCHMENT

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**E**vent-based monitoring of mobile micropollutants in spring water combined with information on their input is used (a) to quantify the impact of certain contamination scenarios on spring water quality and (b) to gain additional information on the intrinsic characteristics of a karst system. The study site is the 45 km<sup>2</sup> rural catchment of the perennial karst spring Gallusquelle (SW-Germany).

We used the artificial sweeteners acesulfame and cyclamate as source specific indicators for sewage along with the herbicides atrazine and isoproturon for agriculture. The combined evaluation of the persistent compound acesulfame with the rather degradable cyclamate allows for the distinction of long and short transit times and thus slow and fast flow components. The same applies for atrazine (persistent) and isoproturon (degradable).

During low flow conditions only atrazine and acesulfame were quantified in the spring water. After a recharge event without sewage overflow, concentrations as well as mass fluxes of both compounds decreased, reflecting an increasing proportion of event water in spring discharge. A breakthrough of isoproturon indicated the arrival of water from croplands. After a recharge event accompanied by sewage overflow, cyclamate was detected at maximum concentrations of 28 ng L<sup>-1</sup>. Simultaneously, the variations of acesulfame concentration suggest the superposition of background dilution (old component) and a breakthrough (fresh component). The cyclamate breakthrough was successfully simulated with a 1-D-transport-model. The application of micropollutants as indicators is suggested as a very sensitive tool in karst hydrogeology, where natural background concentrations and signal damping are often limiting factors for conventional hydrochemical investigation.

## INTRODUCTION TO THE SAN JUAN BAY ESTUARY SYSTEM

The San Juan Bay Estuary (SJBE) System consists of a busy shipping harbor, a series of lagoons and canals, and a diverse tropical ecosystem. The flora and fauna include coral, sea grass, mangroves, and rare or endangered fauna including the Peregrine Falcon, the Leatherback Turtle, and the West Indian Manatee. Surrounding this sensitive ecosystem is the highly urbanized city of San Juan, home to the 2nd largest port in the eastern United States (second to New York City).

In 1992, the EPA added SJBE to the National Estuary Program to help protect and restore this valuable resource; it is the only tropical estuary in the program. The priority issues identified in the Comprehensive Conservation & Management Plan include (1) flushing capacity, (2) illegal sewage discharges, (3) contamination, (4) debris, (5) ecosystems, and (6) public awareness. The contributing watershed is >250 km<sup>2</sup> and includes forests and wetlands in addition to the urban and industrial areas. The population density varies greatly and ranges from 94 to 3215 people/km<sup>2</sup>.

Two field trips will provide an opportunity to learn more about the SJBE. Both trips are led and organized by Excursiones Eco a small local company that was birthed from the community groups involved with the dredging plans for Caño Martín Peña – the canal linking Laguna San José and Bahía de San Juan. The neighborhoods surrounding this Caño have united to provide a public voice in this process and to improve the environmental and public health of their communities. Both field trips are an opportunity to learn more about the health of the estuary and how community groups have responded to the problems and proposed plans.

The “Boat Tour” will provide the opportunity to see San Juan, the bay and the lagoons from the water and observe the local flora and fauna. For this trip you will be traveling with local residents in fishing boats. The “Community Tour” is an opportunity to visit several locations to see restored and contaminated sections of Caño Martín Peña and to learn more about the grassroots involvement in the project.

Following an introductory lecture at 1:00, the field trip will leave the hotel at 2:00 p.m. and will return at 5:00.



San Juan Bay: Google Earth Image



# GUIDEBOOK TO THE KARST OF PUERTO RICO

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## INTRODUCTION

This itinerary is for a bus ride west from San Juan to the Camuy and Aguada karst blocs, with a possible visit en route to the Ojo de Agua spring of Vega Baja. This will be followed by a long stop (and lunch) at the Río Camuy Cave Park to tour the cave, and view the Cueva Clara and Tres Pueblos entrances. Finally, Cueva Minga will be visited prior to the drive through the karst to our hotel in Isabela for the night.

The next day, we will follow a different route through the karst in the gorge of the Camuy River, in transit to the famous Arecibo Observatory, sited in the largest cockpit on the island. We will stop at the former commercial cave of La Luz, prior to an en route visit to the impressive vista from Cueva Ventana alongside the Grande de Arecibo as we make our way back to San Juan. Stops will focus on the evolution of the Puerto Rican karst with its “tropical karst” morphology and coupling to lithology, and hydrologic concerns of quantity and quality.

Puerto Rico is the easternmost large island in the Greater Antilles (Fig. 1). Its known caves (except coastal features) are almost entirely solutional. Although basalt is the most common rock here (and includes pahoehoe), no lava tubes

have been reported: the most recent flows are early Eocene in age. Briefly, Puerto Rico originated as Jurassic seafloor lavas on the western coast of South America, and migrated eastward with the Caribbean tectonic plate before the closure of North and South America. Currently it is at a subducting margin with the Atlantic plate, with its size increased by fringing carbonate accretion. Recent plate compression has arched the island exposing plutonic and metamorphic rocks and likely contributing much of the jointing in the carbonate rocks: nearly all of the karst of PR is developed on rocks of Tertiary age (Fig. 2).

Karst terranes are widespread throughout the Caribbean and flanking areas. A long-standing and unresolved discussion concerns the extent to which climate has dominated in the development of “tropical karst” such as cockpit and mogote and cone karst. These geomorphic terranes are not represented in the United States, but are well-known and well-developed in Puerto Rico. Puerto Rico also contains many areas of less-rugged karst terranes that would appear more familiar to U.S. geologists, and is therefore well-situated for a stimulating and hands-on discussion of karst processes in general. Karst aquifers are an important water resource here, especially in northern Puerto Rico (Miller, 2009).



Figure 1. Tectonic Setting (from Palmer and Palmer, 2009; p. 324)



Age		Formations		Descriptions
Pliocene		Emergence of carbonates above sea level		
Miocene	Late	Quebradillas Fm. Uplift along four sides of island		Sandstone, limestone and sandy chalk
	Middle	Arching causes older Tertiary rocks to emerge and the north coast submerges.		
	Early	Aymamón Ls.		very pure chalk
		Aguada Ls.		hard, stratified limestone
		Upper member		soft limestone
		Cibao Fm.	Montebello Ls.	Mudstone unit
Oligocene	Late	Lares Ls.		thin to thick bedded limestone
	Middle	San Sebastián Fm.		thin bedded sand, clay and some sandy limestone. unconformity sedimentary and intrusive
Cretaceous to Eocene		volcanic		

Figure 2. Stratigraphy of the middle Tertiary, north Puerto Rico. (from Palmer and Palmer, 2009, p. 326)

## SUNDAY, JANUARY 31 DAY 1

[Note: A “K#” (e.g. K2.3) will be used to locate features of interest keyed to the km-markers along the many highways we will follow. Local distances are marked in km, while speed limits are in miles per hour. Gasoline is sold in liters; milk is usually in quarts. Route numbers are given as, for example, “PR-2” ]

7:30 a.m. Check In, and board bus.

We will head west from the Condado Plaza Hilton to the caverns of the Camuy River. The first two thirds will be on the main highway, PR-22, past karst towers and mogotes formed in Miocene carbonates. At the city of Arecibo, we will turn south on PR-129 and gradually ascend both the karst tableland and stratigraphic column to the Oligocene carbonates of the Park.

The Condado and Old San Juan are built on a four-dune complex of carbonaceous aeolianites (probably at least 100 ka BP), case-hardened by rain, solution, infiltration, evaporation and calcite precipitation. The best place to view the cross-bedding is on the sea-level walk around the northwest corner of the El Morro fortress of Old San Juan. Westward along the Atlantic coast these aeolianite dunes persevere against the waves, forming either offshore islands or numerous tombolos (Kaye, 1959).

~K2.0: Soon after we enter the PR-22 toll road, the large mound you see to the north (right) side is a de-commissioned

landfill, now used for driving golf balls. The steep green-covered hills are limestone mogotes, of late Oligocene to Miocene age, which rest on older Tertiary siliciclastics [15 km east of San Juan another grouping of these small mogotes marks that limit of the karst]. To the south (left) a couple of kilometers is the archeological site of Caparra, the seat of government during the (unelected) administration of Governor Ponce de Leon.

K7.3: We pass a large white building (prison) (green metal sign on the right-side shoulder) and with a rapid glance at a 45-degree angle you can see the low buildings of the US Geological Survey. This unit in Puerto Rico is dominantly water-focused.

K11.7: We cross the artificially-straightened estuary of the Río Bayamón, and continue in between lines of mogotes (E/W strike ridges) of the Aguada and Aymamón Limestones.

~K16: As the road outcrops show, these rocks are often orange-yellow-red colors. We are kept at a distance of about 6-7 km from the coast because of numerous large lagoons and swamps developed back of the many aeolianite coastal hills. Numerous springs occur in these sites as inland aquifers discharge after encountering denser salt water.

K22: Just after the first toll booths (and just a few meters above sea-level), Río de la Plata is the first of several large rivers we will cross. At 97 km, it is the longest river in PR. About 3 km up-river is the large spring of Maguayo, one of the PROTECT monitoring sites. It emerges from the Aguada

Limestone.

K24.5-26: Aguada Limestone (Ta) outcropping on the south side in a quarry, and north side in a rock exposure. The hills are capped with the Aymamón Limestone (Tay), (Fig. 3) which forms all the bedrock hills as we rise to 50 m elevation, and shares the large flat areas with the Blanket Sands. These are thick siliciclastic deposits of orange to red sandy clay that Monroe, (1976) describes as being transported here by wind, streams, and possible longshore drift. After a few km we descend to the wide floodplain of the meandering Río Cibuco, ~10 m a.s.l.(above sea level).

K32: Carmelitas Caves Just before the Río Cibuco, we cross PR-2 which ascends north to a 50 m a.s.l. platform with 30 m-high mogotes in the Aymamón Limestone. This is where the low-cost housing development of Monserrate was constructed in 1972, over the known Carmelitas Caves (Monroe, 1976; 66). The caves have at least 37 entrances – some say more – that connect underground from street to street, into which the septic tanks drain, and most of which are plugged with trash (up to 10 m deep), a classic rural and urban usage worldwide (Fig. 4). The caves all seem to share a common flat clay floor. The Cibao-Aguada contact here is at 80 m below sea level.

K 34-35: Meanwhile, back on PR-22, we continue west along the floodplain of the Río Cibuco, then climb up across the Aguada Ls. to 35 meters of exposed Aymamón hills and Blanket Sands. Numerous shallow caves/ shelters are hidden



Figure 3. Aymamón Limestone. Photo by T. Miller.



Figure 4. Septic tanks emptying into Carmelitas Caves, and cave interior 10 m rubbish column. Photos by T. Miller.

in the vegetated mogotes, perhaps uplifted sea caves. A large bridge crosses the Río Indio and not far beyond is the K38 exit where we are likely crossing part of the catchment area of the large Ojo de Agua spring of Vega Baja, another of the monitoring sites of the PROTECT project. (Fig 5). From here to Quebradillas, we are into the holokarst area of northern Puerto Rico, where the absence of surface drainage is striking (Fig. 6).

K34: Be ready (south side) to view the cave opening alongside the road in completely-denuded limestone. Both the Cibuco and Indio rivers carry substantial groundwater flow from the south through caves and impressive karst mogotes developed in the Aymamón, and 2 km further south in those of the Aguada Limestone. These latter mogotes are in the borough of Pugnado Afuera, which has appeared in a popular air photo of many US geology/geography texts as an example of mogote topography (though not always sharing the same compass orientation...).

This region between the Cibuco and the Río Grande de Manatí has been titled the Cibuco Karst Block (Fig. 7). As





Figure 5. Ojo de Agua spring of Vega Baja. Photo by T. Miller.

with the three other karst blocks to the west, it is bounded by rivers into which the karst discharges.

K39: The valley surface is a topography seemingly subdued by the presence of the Blanket Sands, which are seen (north and south sides) filling a couple of grikes in roadside exposures. The wide valley surface is at ~80 m, perhaps related to an extensive series of knickpoints in streams and caves at similar elevation to the west (Troester, 1994; Miller, 2009).

The highway travels here enfilade between long chains of resistant beds outcropping on E-W strike-oriented hills almost 100 m tall (Fig. 8). As with most of the Tertiary stratigraphy of the north coast, the rocks dip gently north at about 4-5°. There are no surface streams between here and the city of Manatí to the west: after they have formed on the low-permeability silicates and carbonates of the Cibao Formation to

the south of us, they are captured by about a dozen numerous swallets of the Aguada Limestone located along the 9 km contact front (Figs. 9-10).

K50.7-54.3: The large river we cross (annual mean discharge 454 cfs) is the Río Grande de Manatí. Upstream can be seen the 200 m walls of the gorge cut through the carbonates as the island rose out of the sea. The limestones exposed here are 20 km wide N-S. Ten km south, on the west bank, is Aguas Frias, the largest resurgence on the island, where the well-known caves of Sistema Río Encantado pour into the Río Manatí. Episodically cut to bedrock, the mouth of the Manatí has filled with about 120 meters of alluvium with the most recent sea-level rise (decreasing upstream), and the drowning pre-existing karst drainages developed during glacial periods. The conduit of Encantado itself briefly dips below sea-level, 15 km from the coast. Currently, the long underground stream course is split into 18-km and 4-km sections separated by an unroofed slot canyon, with a total vertical relief of about 350 m. (Miller, 2010a; Miller, 2015).

K52.8: As a historical commentary, downstream, north across the wide floodplain, are three tall chimneys, remnants of the sugar cane era. The valley here was once filled with sugar cane mills and facilities for heating and thickening the sugar molasses. These haciendas were still in full operation when I visited in the 1970s.

K57: On the other side of the Manatí, we enter the Florida Karst Block (note dissected mogote on the left). The highway exit provides access to the main area of the island's pharmaceuticals industry (it should be noted that the town of Ciales to the south has no more than a misspelled relation to one of the chief drug products).

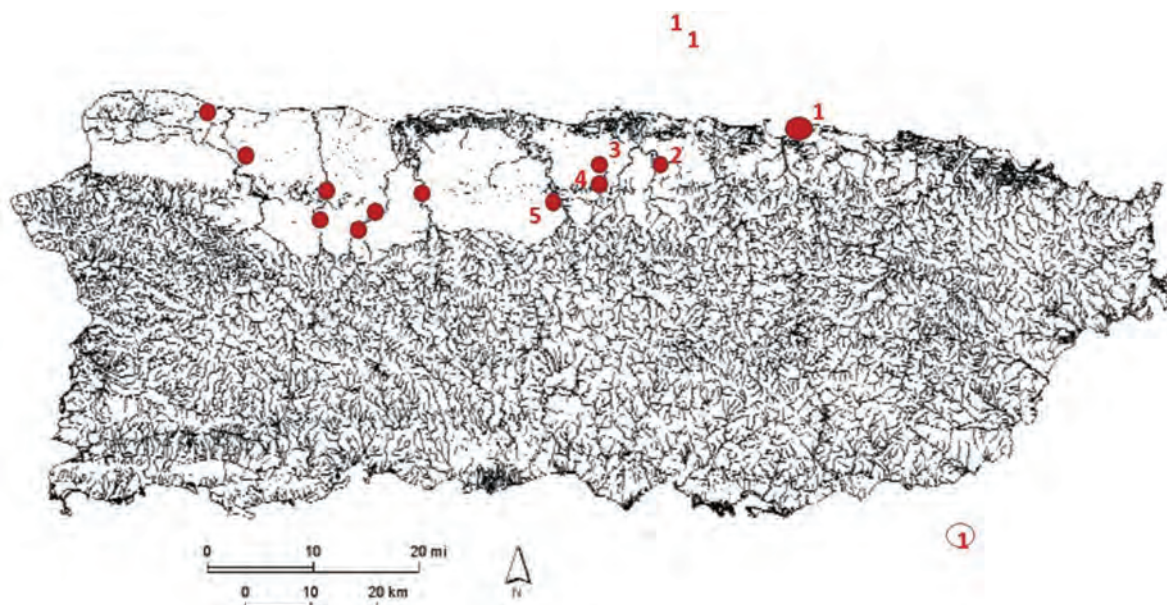


Figure 6. Surface streams and channels of Puerto Rico. From Lugo et al. (2001; 2). USGS data base.



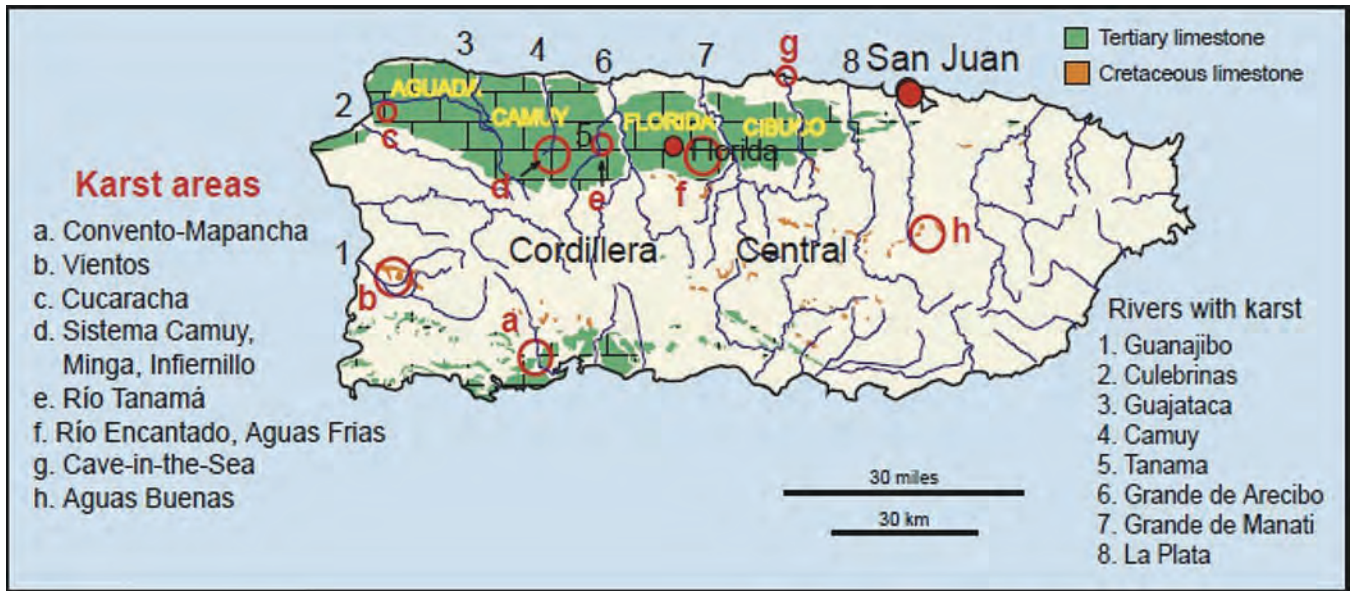


Figure 7. Karst Divisions of Puerto Rico. From Miller, (2009; 325)

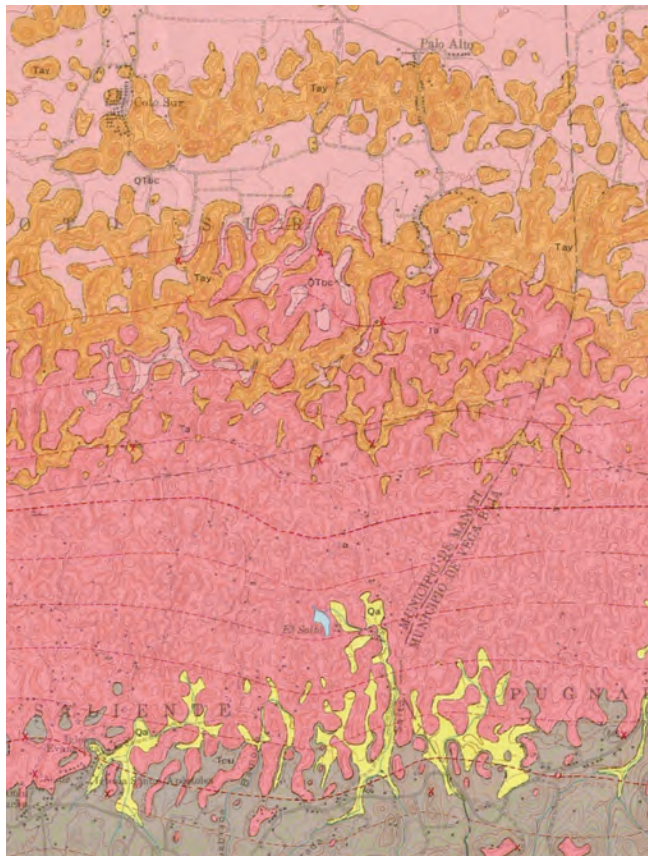


Figure 8. Mogote hill-chains, following E-W strike.



Figure 9. Ponor of Quebrada Hicatea. Photos by T. Miller.

K60: One of the more notorious local chemical spills occurred in 1982 on PR-2 when "...an estimated 15,300 gallons of waste material containing 65% CCl<sub>4</sub> and 35% acetonitrile leaked from [an] underground tank..."(EPA, 1999).By 1987 the plume was one km wide, and had flowed northwestward about 3 km, mostly within the Blanket Sands. It was treated successfully using air-stripping and a pumping-produced piezometric barrier.

K59-60.4, and 61.8: There are several good views of mogotes in the distance to the south.

K63: The large landfill of the city of Arecibo is visible distantly north, look quickly. It is located in one of the larger coastal wetlands of the island.

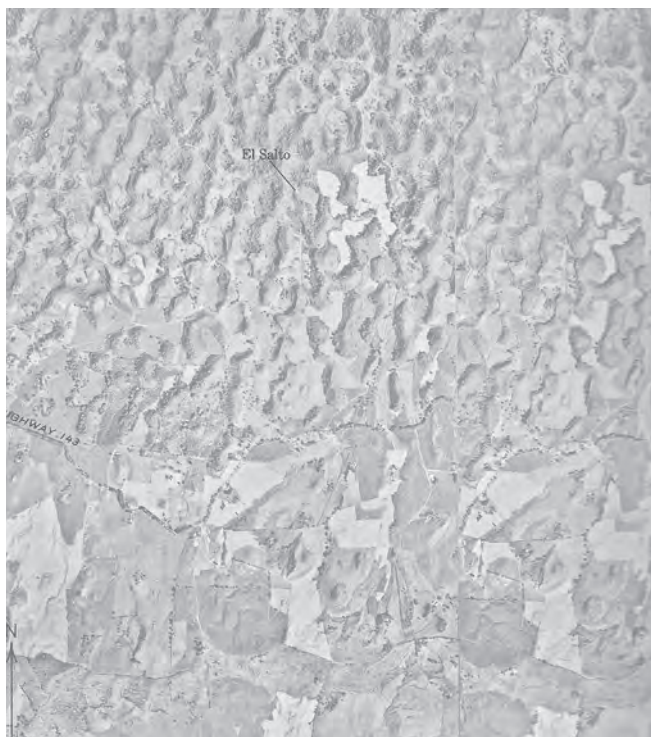


Figure 10. El Salto polje: sinking of stream in Aguada Limestone, after forming on Cibao Formation. From Monroe (1976: 30).

K65: A possibly apocryphal observation is that asymmetry exists in the profile of the mogotes (rising from the east to a steeper west side), attributed to case-hardening by the north-eastern tropical source of the local winds (Monroe, 1976; 44-45). However, when Day (1978) actually measured mogotes in the Miraflores area, several kilometers to the south, he found asymmetrical mogotes, but with no single significant orientation. He calculated “tower summit densities” of ~18-30/km<sup>2</sup> in four different areas.

K69: If you haven’t yet spotted the blue and gold pipes of the Superaqueduct (“SuperTubo”) they are visible at south roadside in the area of K69 and other places. They are part of a system that transports up to 75 mgd from the Río Grande de Arecibo ahead of us, eastward to the western outposts of the metropolitan area. The Aymamón is still the bedrock along the roadside, although now some of the mogotes are capped with thin layers of the Quebradillas Limestone (Tq; previously called the Camuy Limestone.); it is the youngest limestone, of Pliocene age. Although porous and permeable, it rarely contains enough water to function as an aquifer. The surface of most of the flat areas here is the familiar Blanket Sands.

K75: The crossing of the Río Grande de Arecibo, the largest of Puerto Rico’s rivers (annual mean flow 495 cfs), meandering in a broad flat valley of oxbows and cutoff lakes through its 200 m deep gorge. The Río Tanamá is visible as a smaller gorge in the hills on the west side. Compared to the

mean discharge of the Arecibo, the Tanamá discharge at 106 cfs is unable to maintain a surface course and flows through nine separate caves. After crossing the river, we will ascend through outcrops of Aymamón- and, for the first (brief) time, the Quebradillas Limestone to road PR129 and the large municipal cemetery of Arecibo.

~K78: Here we leave PR-22. The last of the big coastal swamps and lagoons is behind us and there is now access to the coast. We will head SW from the city of Arecibo, turning south on PR-129 and then gradually ascend both the karst tableland and stratigraphic column to the Oligocene carbonates of the Camuy River Caves Park. This is also the last view of the Quebradillas Limestone until we reach our hotel tonight.

The E-W strike-oriented lines of hills of Aymamón Limestone, 30-50 m high, span nearly the length of a quadrangle map. In between are level expanses of the Blanket Sands. From sea-level, the platform rises to 300 m and then crosses the Aguada and into the Cibao Formation for the first time and then into the Lares Limestone before reaching the Camuy Caves. Distances on this road are sometimes estimated due to the small size and scarcity of kilometer-posts.

~K7.5: PR-635 leads east from here into a warren of roads, eventually to the well-known Mata de Platano Field Station, where innumerable bats roost in one of the island’s “hot caves,” and are captured and eaten by boas as they exit. <http://fieldstation.azurewebsites.net/>

K8.5: Tony’s Pizza (east side), unofficial after-the-meeting site of the Arecibo cave club “SEENI” (Sociedad de Estudios Espeleológicos del Norte, Inc.)

~K10: Rare bedding visible on west side of quarry and cement business. Cliffs of Aymamón Limestone above Aguada Limestone.

K18.9: Parque Nacional Cavernas del Río Camuy (Camuy River Caves Park)

<http://www2.pr.gov/Agencias/cdpn/cavernas/Pages/default.aspx>

11:00a.m. -1 p.m. The large Camuy caverns (Fig. 11) are one of the major tourist attractions of Puerto Rico. We will have prime access and view features not usually available to the general public, such as the immense Tres Pueblos collapse (Fig. 12) and the Espiral entrance.

Modern exploration of the Río Camuy Caverns began in the late 1950’s under the leadership of Russell and Jeanne Gurnee. The present park largely represents the acreage they initially purchased to use as a basecamp. Surveying mostly commenced in the 1960’s (Gurnee and Gurnee, 1973) with the length of the cave increasing as decadal pulses of new discoveries were contributed in the 1970’s, 1980’s, and



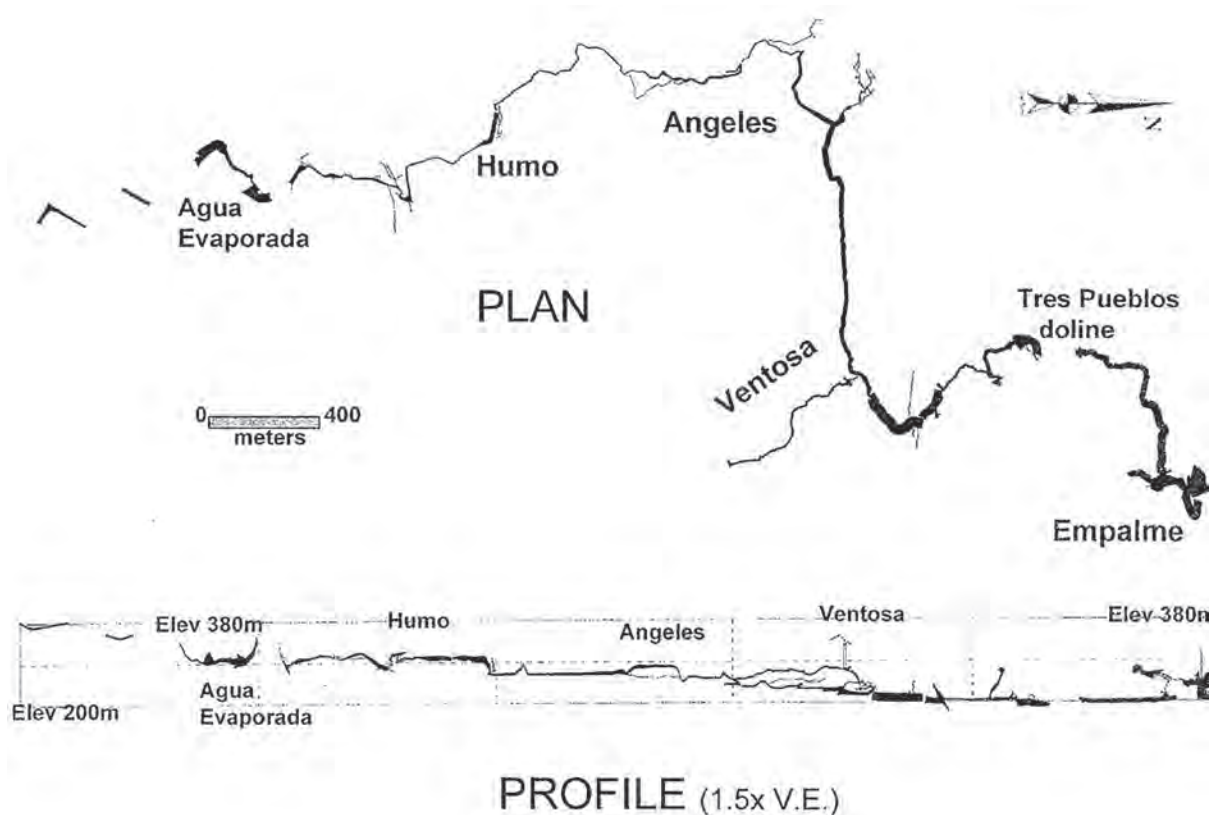


Figure 11. Current map and profile of the Río Camuy cave system 1972-2015, by numerous surveyors. Drawn by T. Miller.

2005-2015. Two detailed theses addressed the entire system, especially including the resurgence area and the hydrology (Torres et al. 1984), and the vertical profile along the main trunk (Troester, 1994). The latter described and interpreted the presence of four major “levels” or galleries (large discrete passages along the same gradient path). These were discarded sequentially as newer conduits were discovered below each prior base level, and abandoned segments were found scattered across the plateau. Recent cosmogenic studies of Camuy cave sediments (Brocard, Willenbring, Miller and Scatena, in review) support the assertion that the Camuy conduits were fully developed by about 5 My BP, not long after the Luquillo mountains of eastern Puerto Rico had uplifted from the surrounding shallow seas (Brocard et al., 2013; Brocard et al., 2015).

A complicating factor is that the Camuy system is developed in two soluble units – the Lares Limestone and the Cibao Formation – with a large gap in known passage between them. The Río Camuy is organized on basalts and volcanoclastic sediments of Cretaceous age, then flows north across a long polje to sink in a large bamboo-and plastic bottle-choked ponor in the Lares Limestone (it’s worth noting that bamboo was introduced to Puerto Rico about 90 years ago).

Our tour will enter Cueva Clara (Fig. 14) at the north of the entrenched collapse representing one of the ancient routes of

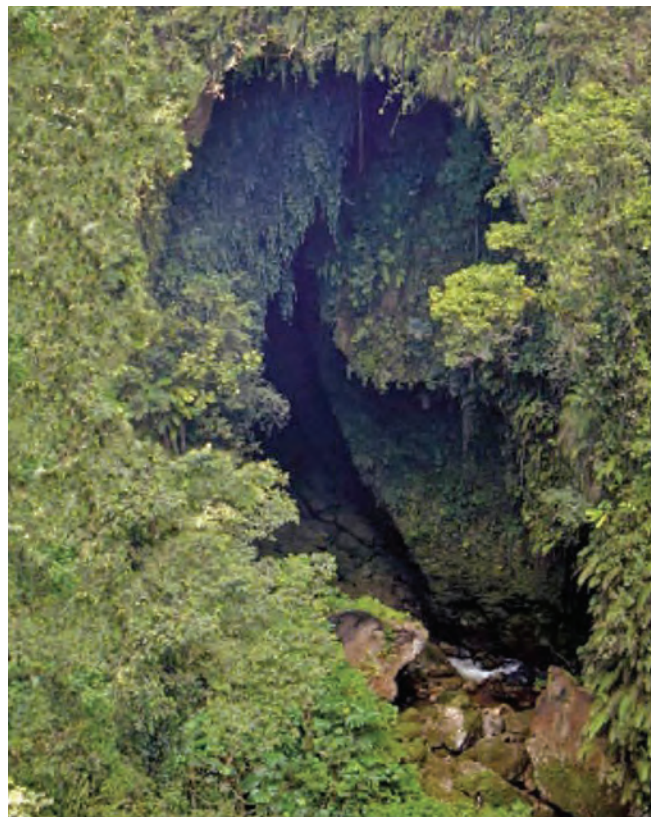


Figure 12. Tres Pueblos 100m collapse into the Río Camuy cave system. Photo by T. Miller.





Figure 13. The ponor – sink point – of the Rio Camuy. Photo by T.E. Miller

the “classic” Camuy caves (Fig. 15), and pass through large chambers to emerge in the impressive Sumidero Empalme, a 120 m deep pit that pierces from the surface to the modern Río Camuy streamway below. We will encounter the pit about 30 m up the side. The passage appears to have connected to a large opening visible across the pit, but which is short and marks both the termination of the southern section of passages and the approximate start of the Cibao Formation. Numerous caves exist between here and the resurgence, about one km distant, but most are relatively small and prone to flooding. Mean discharge of the Río Camuy at the gage a little north of the resurgence is 115 cfs.

During the 1998 Hurricane Georges, the river back-flooded to the level of the tourist trail. The caverns are a natural flood-control feature, protecting the large town of Camuy on the Atlantic coast while limiting most flood discharges to <8,000 cfs. (although the Georges flow reached 12,000 cfs). Mean flow of the Río Camuy in the tourist cave is only half of that at the gage to the north. The source of this additional flow is not yet identified.

After departing from Cueva Clara, we will travel to the huge Tres Pueblos collapse, a feature similar to the Sumidero Empalme, but on a larger scale. The river is visible below, entering and departing the bottom en route to Cueva Clara. This is a part of the park no longer seen on most tours.

There are washrooms here, and it is likely where we will have a box lunch. Those who eat quickly can make a hasty dash down the wooden boardwalk to peer into the Espiral Entrance pit of the main cave.

1:00 p.m.: After Tres Pueblos and lunch, we will head south-east, passing Cueva Golondrinas, one of the unconnected Cibao unit caves. Like other easily accessed karst depressions, it contains scores of used tires, mattresses, dolls, license plates,



Figure 14. Cueva Clara, the commercial tour of the Camuy caves; view out to the Empalme pit. Photo by T. Miller.

and a surprising number of unbroken Heineken bottles at the bottom of its 40 m entrance pit. From here we drive south through the rolling landscape of the Cibao, then well into the impressive mogote and cockpit karst of the Lares Limestone. From one to several kilometers east of the highway are numerous conduit cave fragments of previous routes of the Río Camuy and others that appear to have developed independently. About 1.5 km to the SE is where the Río Camuy sinks.

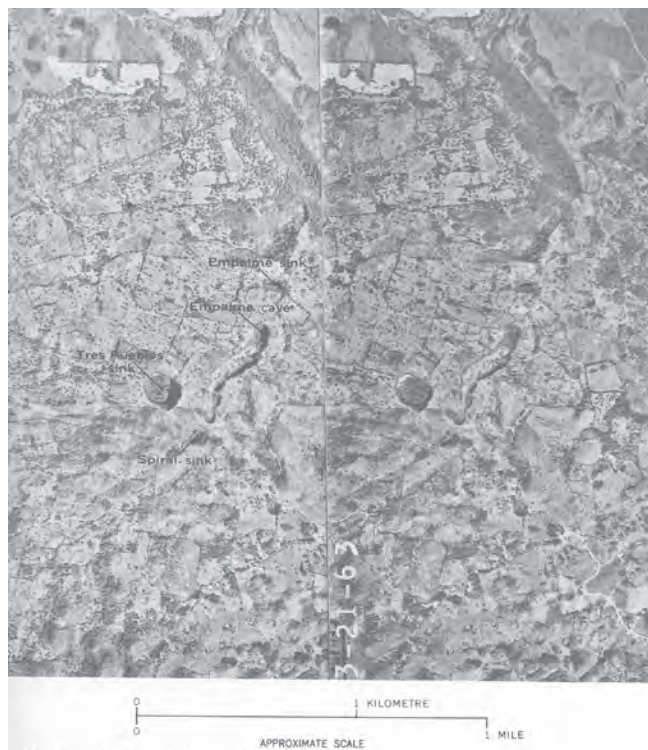


Figure 15. Stereopair of aerial photographs above part of the Río Camuy cave system showing Tres Pueblos pit, and the collapsed trench leading to the Empalme Entrance. From Monroe (1976; 35).

Older passages further south were part of the E-W strike conduit that merged with the Río Tanamá to the east (Miller, 2010b). About 4½ My BP the Camuy drainage rotated north and has traveled independently down-dip since then.

~K22: Cueva Minga (Entrada Petraca)

Formed in Lares Limestone, this is essentially a block maze of about 1000 m surveyed cave developed on two levels, on perhaps two joint sets (NW-SE and NE-SW), and once largely filled with clay (Fig. 16). There is a small ephemeral stream at the extreme south end, probably a simple surface capture as there is no evidence to suggest anything other than phreatic development in Minga. At some earlier time it has been largely excavated, probably for fertilizer, especially a phosphate-rich cap on the clays. This has made the enlarged passages easier to navigate (Fig. 17). Most speleothems and drips are restricted to the north end because the cave passes south underneath an impermeable cap. In this section near the entrances there are a few bats, roosting in the many bell-holes in the white, weathered ceiling. The brown streaks coming out of the bellholes are variants of the phosphate mineral apatite, formed by reaction of the bat guano with the host rock (Fig. 18).

This is a wild cave, so a helmet, lighting, boots and appropriate clothing are needed. A couple of handlines will be installed to ease some short sections.

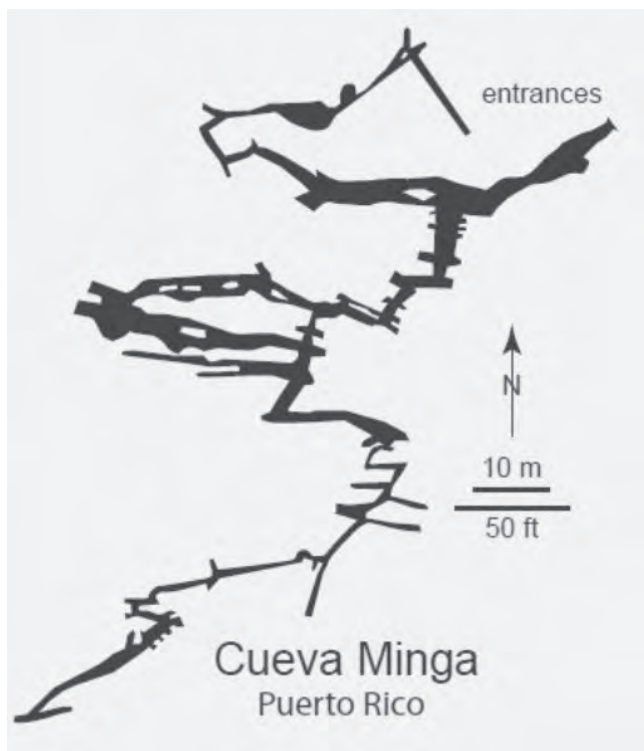


Figure 16. Map of Cueva Minga, a block maze. Drawn by T. Miller.



Figure 17. View of typical excavated passage in Minga. Photo by T. Miller.

3-3:30P - 4:15-4:45P: Drive to Isabela and hotel

PR-454 - PR-455 will take us immediately across the moderately rugged terrain of the Montebello Limestone (Tcm) of the Cibao Formation. This unit produces some mogotes and stream caves. PR-455 runs east/west here, marking the contact with the marly/sandy Cibao (Tc). North of this line, surface streams are able to form and flow down dip into a hard limestone layer near the top of the Cibao, where here and elsewhere on the island swallets produce some of the major caves of Puerto Rico. After a short run west, we turn north, crossing the Cibao, and enter the cockpit karst of the Aguada Limestone, now divided into upper and lower members. Level lowlands are sprinkled here with Blanket Sand deposits, and after a few kilometers of this, hilltops are increasingly topped with thicker Aymamón Limestone which is the bedrock exposed by the time we merge with PR-119.

K15.3: PR-119: to cut off on PR-113.

K16.3: PR-113 heads to the town of Quebradillas. All the level lowlands here, between E/W strike ridges of Aymamón, are Blanket Sands. PR-113 follows the subdued blanket sand topography to our second view of the rolling Quebradillas Formation [Tq, Oligocene].

It is not common to recognize structural features in the north coast limestones, but Quebradillas is built on a small anticline/syncline feature. "Ancient beach deposits" are found on uplifted marine terraces 50-70 m a.s.l., into which ravines and small gorges have entrenched (these are known as quebradas or quebradillas, in English: "breaks").

K102: Infilled grikes are visible in the sides of the roadcut. The Quebradillas Fm. is less than 60 m thick here, and the Aymamón Limestone reappears as PR-2 descends to cross the Río Guajataca. The river is one of the few streams of moderate discharge in Puerto Rico that crosses the karst without diversion underground. The flow here is usually quite





Figure 18. Bellholes and a bell basin, bat erosion features developed in a passage in Puerto Rico. The brown streaks on the bellholes are variants of the phosphate mineral apatite. Photos by T. Miller.

small, due to constant diversion of about 30 cfs into a system of canals. Since the 1920s they feed water to the extreme NW part of the PR karst. Upstream, the Guajataca flows in narrow floodplains developed in entrenched meanders. Of special interest are the presence of “ramparts,” large natural levees of limestone that rise to more than 155 m along the river sides, then descend 35 meters to flat blanket sand-cov-

ered rock on either side. Monroe (1967; 39) attributed these to “sheet solution” beneath the sand, and case-hardening of the adjacent soft porous limestone. They have been noted elsewhere in Okinawa and Guam.

Visible to the west as we cross the river is a tunnel of the old Puerto Rican railroad, abandoned in 1953. The rails circumnavigated the island and served both sugar cane and passenger cargo for decades before that. We climb back to the plateau on the west side, variously crossing Aymamón and Quebradillas limestone, often covered by the Blanket Sands.

Our hotel lodging is at Isabela, a large town built on ancient cross-bedded calcareous aeolian dunes (about 20 m thick on an uplifted terrace) overlooking the Atlantic. As we descend the scarp to Costa Dorada Beach Resort & Villas, numerous other younger case-hardened dunes connected by tombolos to the main island are visible, and make fine sheltered swimming beaches within easy walking distance.

## Monday, February 1 DAY 2

Itinerary Isabela to Parque Camuy:

7:30 a.m.: Board bus. We will pass through the Parque Camuy area en route to the Observatory. First, we will drive east on PR-2 mostly on tectonically-uplifted low hills of the Quebradillas Limestone (viewing sea caves developed on one of these terraces) and/or through mogote chains of the Aymamón Limestone.

K91.1: Watch the roadcut walls for more sinkholes filled with red blanket sands.

K89.1: We cross the Camuy River, flowing in entrenched meanders south of us, with small floodplains, and sides initially 50 m high, gradually increasing upstream to in excess of 100 m. Ramparts are not present, but a few hills at the sides of the river gorge are sometimes higher than the adjacent sheet areas of blanket sand.

After crossing the Río Camuy near its mouth, we’ll turn southeast on PR-130 at Hatillo to parallel the stream across blanket sands with some mogotes and ridges. Initially we’ll climb a couple scarps of what appear to be marine terraces to top out on the plateau, in Quebradillas Limestone.

K3.9: This is a rolling area of cows and pastures, and if you’re attentive you can smell the “dairy air.” After entering another mogote-chain/ Blanket Sand terrain, we continue south to K8.0, PR-488 and turn west to the hamlet of La Cuesta, right at the start of the Aguada Limestone. The road descends to the gorge of the Río Camuy (K7.5) between high cliffs of Aguada Limestone, which as we go upstream becomes floored with strata of the Cibao. We’ll follow the



turbid waters of the Camuy upstream past (K6.5) the “Boca de Infierno,” (Mouth of Hell) a major resurgence of a large cave system in the upper Cibao Formation.

K4.8: The USGS gage of the Camuy downstream of its resurgence from the caves is visible on the left, and (K0.9) left, a broad panorama of the karst we pass to arrive back at the Parque Camuy.

## SITES WE WILL VISIT TODAY:

### (SEQUENCE UNKNOWN)

#### *ARECIBO OBSERVATORY*

It is ~22 minutes from the Parque Camuy to the Arecibo Observatory, featuring the 300 m-wide radar dish used to discover pulsars. North several kilometers on PR-129 to the stoplight and junction with PR-134, east past the community of Bayaney to PR-635, then east to PR-625, all of this on less-permeable units of the Cibao (although the several streams we see all sink within short distances). PR-625 leads 4 km south to the Observatory, whose site was chosen as (allegedly) the largest and deepest (60-90 m) cockpit on the island,

a bowl of Lares Limestone surrounded by steep mogotes and cockpits of the Montebello Limestone of the Cibao Formation. (Fig 19). Almost (but not quite) running underneath the observatory is the largest cave of the Río Tanamá.

#### *CUEVA LA LUZ and EL HOYO*

This former show cave in the Lares Limestone is only about 4 km due west from the Observatory, but is almost a half-hour drive. A short 10 minute walk in the forest leads to Cueva La Luz, a single roomy chamber with interesting decorations. From here, another short path leads to the impressive El Hoyo, one of numerous karst features in the area.

#### *CUEVA VENTANA*

2 p.m.: A 10-minute walk will take us to Cueva Ventana, with a dramatic cliff view down into the large valley of the Río Grande de Arecibo, and which is entrenched almost 200 m into the Quaternary carbonates. At least two other large entrances are directly below the cave, but do not have great extent. Ventana is a segment dissected from a larger chamber immediately north of the stairs into Ventana.

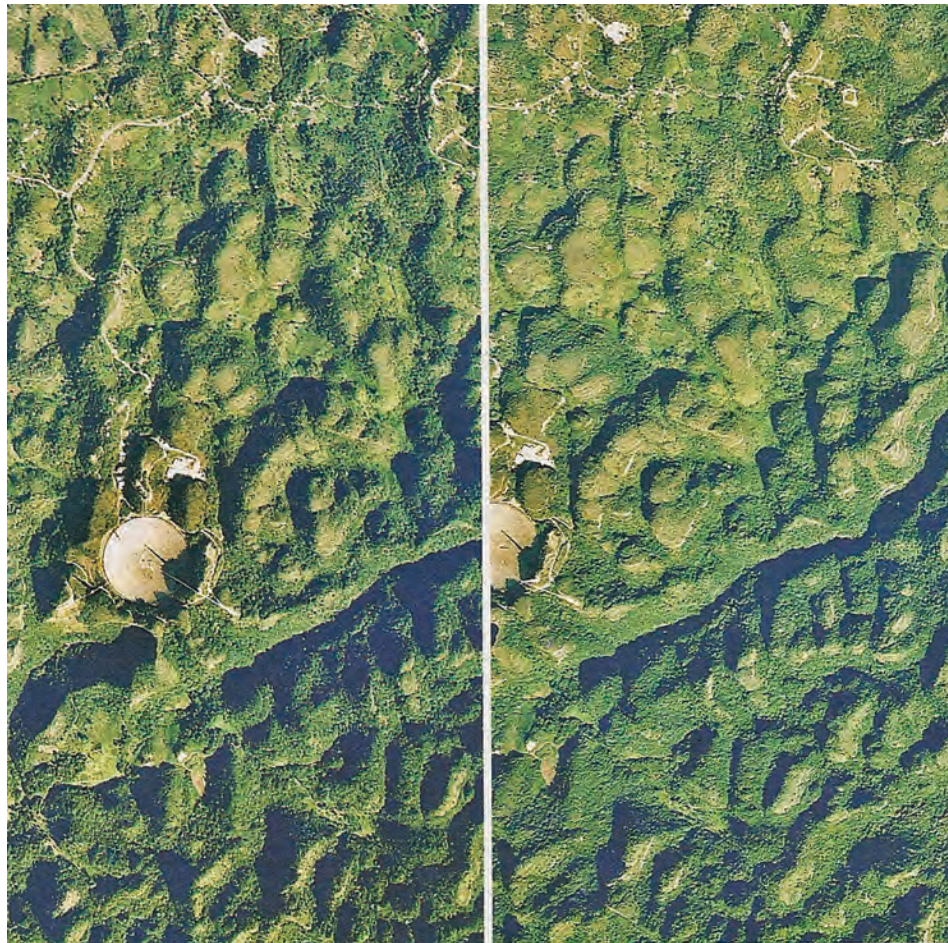


Figure 19. Stereopair of streambank ramparts, rock levees in the northern section of the Río Guajataca, attributed to case-hardening of the adjacent soft porous limestone. Monroe (1976; 39).

*VALLEY OF THE RÍO GRANDE DE ARECIBO*

3 p.m.: Time permitting, after a short drive south to visit to a high viewpoint of the cockpit/ mogote karst, we will descend to the valley floor to view exhumed hills of volcanoclastics, resurgences and uplifted cave entrances, on our way back to San Juan.

6 p.m. Arrival to San Juan

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